Effect of crystal phase composition and morphological properties on the reductive and oxidative abilities of TiO\textsubscript{2} nanotubes

Summary
The main goal was to reproduce TiO\textsubscript{2} nanotubes (TiNT) and explore the effect various parameters had on the nanotubes’ reactive capabilities. I followed a procedure outlined by Baiju K. Vijayan for synthesizing TiNT’s and aimed to reproduce the amount of CO\textsubscript{2} reduction he reported in the literature. In trying to reproduce the reported reactivity, I also varied the calcination temperatures and times to see how that affected the reactivity of the nanotubes in photocatalytic CO\textsubscript{2} reduction.

Synthesis
A previous batch of TiNT made during the school year showed only negligible reactivity, so in the first week I made a new batch and was more careful with cleaning the equipment used, crushing the precipitate, and washing the precipitate. For the vast majority of the summer, I calcined samples from this batch at various temperatures and times for testing.

Though testing was still being done on the second batch, I decided to try synthesizing a new batch on the side to see if doing something different during the synthesis would give improved reactivity. In the synthesis, the precipitate was more finely crushed than done previously to ensure that acid washing was done thoroughly.

Sample Preparation
In the literature, TiNT calcined at 400°C for 1 hour showed the greatest CO\textsubscript{2} reduction followed by nanotubes calcined at 300°C for 1 hour. I therefore started out by calcining the samples at these two temperatures. The calcination times were also discovered to have an effect on the CO\textsubscript{2} reduction so various calcination times (between 1 and 3 hours) at the same temperatures were also used.

Characterization
The methods used for characterizing the nanotubes were X-Ray Diffraction (XRD) and Scanning Electron Microscopy (SEM). XRD plots were taken for all the samples calcined at each temperature. For a TiNT sample calcined at 400°C for 1 hour, an XRD plot of a sample I prepared was compared with a plot from literature. All the major peaks matched up, though there was also an extra broad shoulder peak in my plot. It has been suggested that this peak is insignificant, but it might suggest that something in the synthesis was done differently. Since there are a lot of steps in the synthesis, it's difficult to tell what that might be. SEM pictures were taken for the samples calcined at each temperature as well. Visually, the nanotubes look similar. The average tube radius and average tube length were also similar to the values reported in literature, though the diameters tended to be slightly larger by about 2 nm from the reported average value.

Reactivity
The photocatalytic reduction of CO\textsubscript{2} was used to evaluate the reactive capabilities of the nanotubes. CO\textsubscript{2} was sent into a reactor where a 10 mg sample the TiNT was present and the reactor was exposed to UV light for 3 hours. The amount of CH\textsubscript{4} produced was recorded and compared with values from literature.

It can be seen from the plot of methane production over time that under the same calcination temperature, varying the calcination time can change how reactive the TiNT’s are. From the batch I synthesized in the beginning of summer, it seems that samples calcined at 300°C and for 2 hours were most reactive in the photocatalytic CO\textsubscript{2} reduction experiment.
However, when compared to the reactivity reported in the literature, this is still much less. Methane production of up to 0.8 to 1.6 $\mu$mol/g has been reported, though some of the samples at other calcination temperatures also showed methane production in the range of 0.1 to 0.2 $\mu$mol/g, which are similar to my results.

There was not enough time to do much testing on the newly synthesized batch but a sample calcined at 400 C for 1 hour (New 400 C, 1hr) seemed to show much greater CO$_2$ reactivity than a sample calcined at 400 C in the previous batch. It remains to be seen if samples from this batch calcined under other temperatures and times can show activity that approaches what is reported in literature.

**Discussion**

There are a lot of parameters at play during a synthesis so it is hard to figure out what I did differently. Further, it is hard to determine whether or not the TiNT I have synthesized are the same or different given the methods of characterization I used.

However, new information can still be learned by sampling the parameter space. Though I was not able to reproduce the level of CO$_2$ reduction reported in the literature, I was able to show that calcination times could also be a decisive parameter in TiNT reactivity. While it is reported in the literature that TiNT calcined at 400 C are more reactive than 300 C, my results show that TiNT calcined at 300 C for 2 hours show higher reactivity than any of the 400 C samples. This suggests that there might not only be an optimal temperature, but an optimal temperature and time combination. TiNT calcined at 300 C are said to have higher surface area but are less crystalline than that calcined at 400 C. However, it has also been suggested that longer calcination times cause the TiNT to be more crystalline. The calcination time thus gives us another parameter to look at when probing the combined effects of TiNT crystallinity and surface area.

A next step could be to characterize the crystallinity and morphology of the nanotubes and draw conclusions about how those two things might affect activity. Transmission Electron Microscopy (TEM) could be used in the future to further characterize the nanotubes and probe the effect that calcination times have on their morphology.