Post Combustion Carbon Capture Using Polyethylenimine Functionalized Titanate Nanotubes (FE0023040)

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Outline

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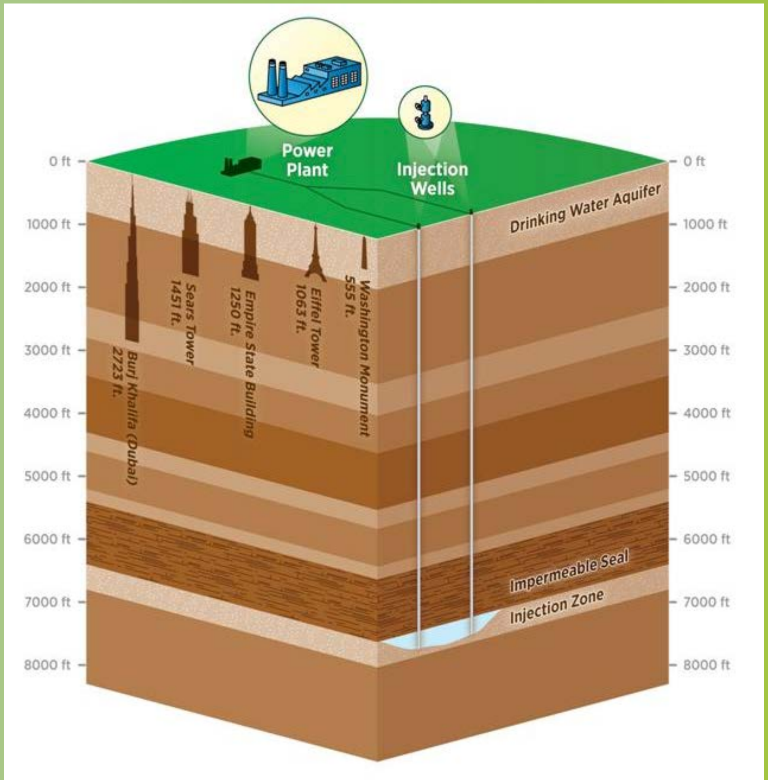
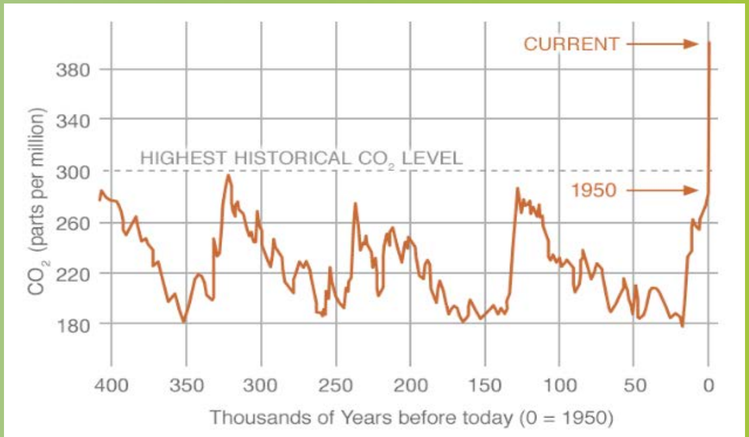
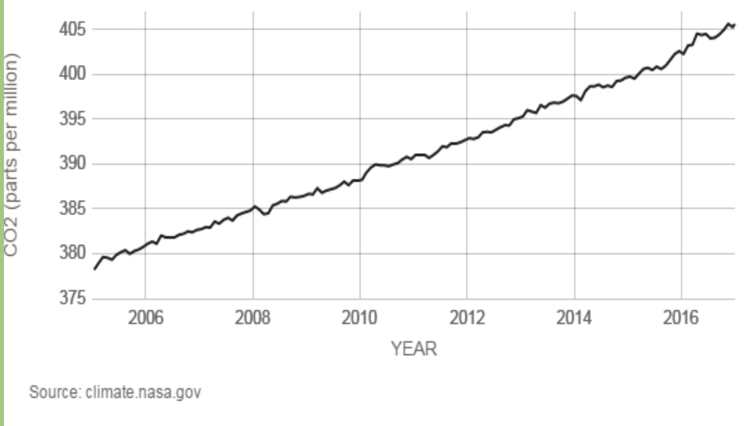


Carbon Capture and Sequestration Schematic
Overview of Greenhouse Gases. (n.d.).
Retrieved February 25, 2016, from
http://www3.epa.gov/climatechange/ghgemissions/gases/co2.html

Introduction: Carbon Dioxide (CO_2)

- Atmospheric CO_2 concentration is about 406 parts per million
- Multiple possible ways for reducing emissions
  - use of low carbon energy sources
    - e.g. natural gas
  - carbon capture and sequestration
    - several ways of capturing carbon
      - absorption using liquid amines such as monoethanolamine (MEA)
      - solid adsorption using polyethylenimine (PEI)

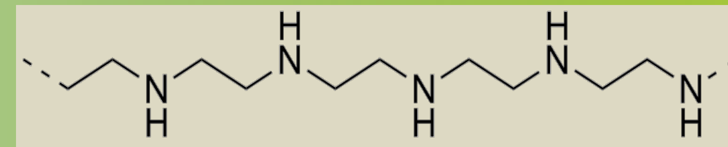


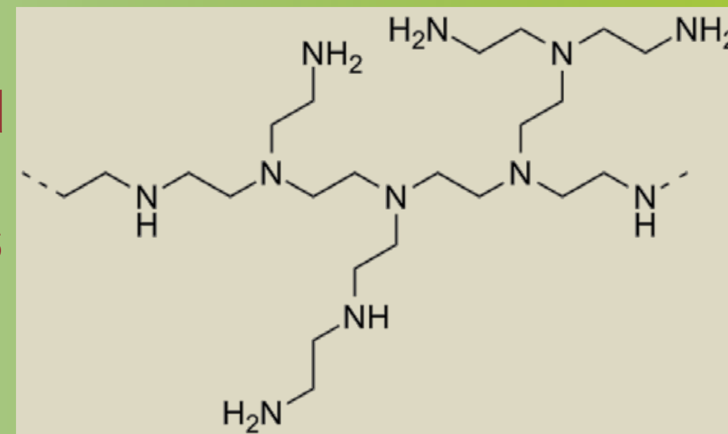


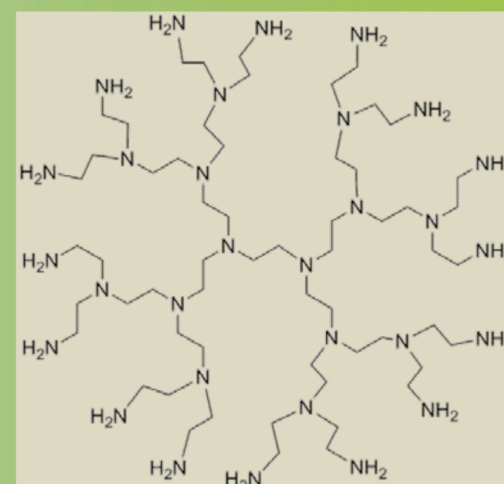
Source: NASA Global Climate Change-Vital Signs of the Planet
https://climate.nasa.gov/vital-signs/carbon-dioxide/
Retrieved on March 1, 2017

Polyethylenimine (PEI)

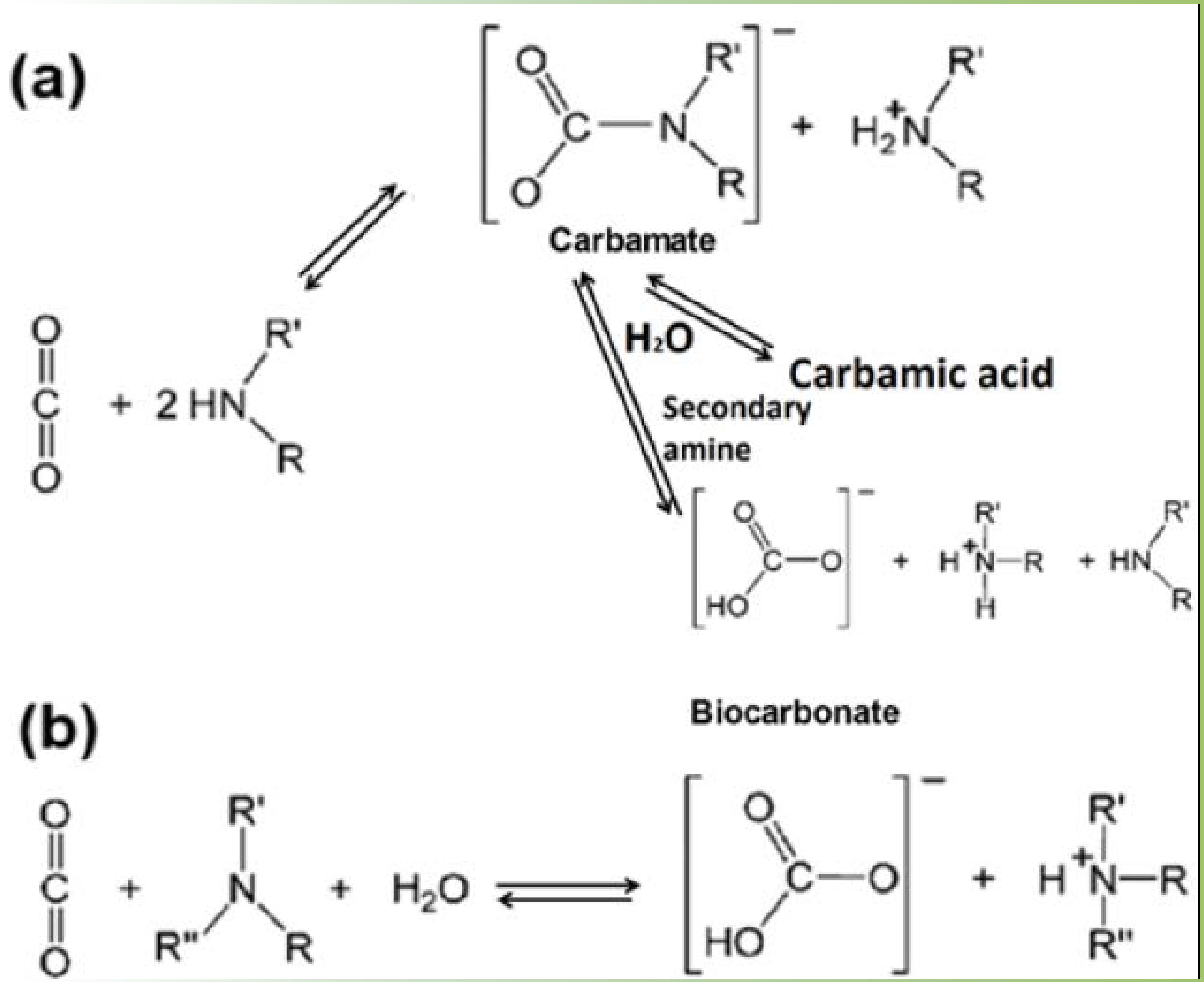
- Polyethylenimine (PEI) is a polymer composed of the many amine groups
  - Can be impregnated, grafted, or directly synthesized on various solid adsorbents for CO_2 capture including porous titanate nanotubes
- Linear PEI fragments
  - All secondary amines
- Branched PEI fragments (used in this study)
  - Primary amine groups(30%)
  - Secondary amine groups (40%)
  - Tertiary amine groups (~30%)
- Dendrimer
  - Primary and secondary amines







Absorption reactions of amines with CO_2



D. M. D’Alessandro et al. *Angewandte Chemie* **2010,** 49, 6058-6082; D.D. Miller, S.S.C. Chuang, *Energy Fuels* ***2016****, 30, 7575-7587*

Adsorption Capacities of Adsorbents

Adsorbent	Adsorption conditions	Reported Adsorption capacity (mmol/g)
IG-MWCNTs-PEI-EC-40		2.141
TiNT-raw		0.78
TiNT-MEA-56		1.25
TiNT-EDA-47		1.42
TiNT-TETA-51		2.87
TiNT-TEPA-43		3.96
TiNT-TEPA-22		2.26
TiNT-TEPA-69		4.37
TiNT-TEPA-91		4.13
Tetraethylenepentamine-Al_2O_3		2.97
Propylethylenediamine-carbon		1.64
Tetraethylenepentamine-MCM-41		4.79
Tetraethylenepentamine-MCM-48		0.68
Propylethylenediamine-SBA-15		1.36
Tetraethylenepentamine-TiNT		4.37
PEI/AC	8% CO_2	1.3
PEI-K_2CO_3/AC	8% CO_2	1.2
PEI/AC	8% CO_2; 12%H_2O	2.4
PEI-K_2CO_3/AC	8% CO_2; 12%H_2O	3.6
SBA-15-PEI 50		2.88
SBA-16-PEI 50		2.93
KIT-6-PEI-50		3.06

Objectives

- Synthesize a novel CO_2 adsorbent of PEI-PTNTs using 600MW PEI, 10,000MW PEI, anatase and P25 powder
- Study the effects of temperature on both the CO_2 adsorption capacity and synthesis of PTNTs
- Characterize samples using X-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM)
- Develop a geometric model for CFD simulation with a central porous section that represents the packed bed adsorption section
- Evaluate the viability of PEI-PTNTs as adsorbent for CO_2 capture from flue gas

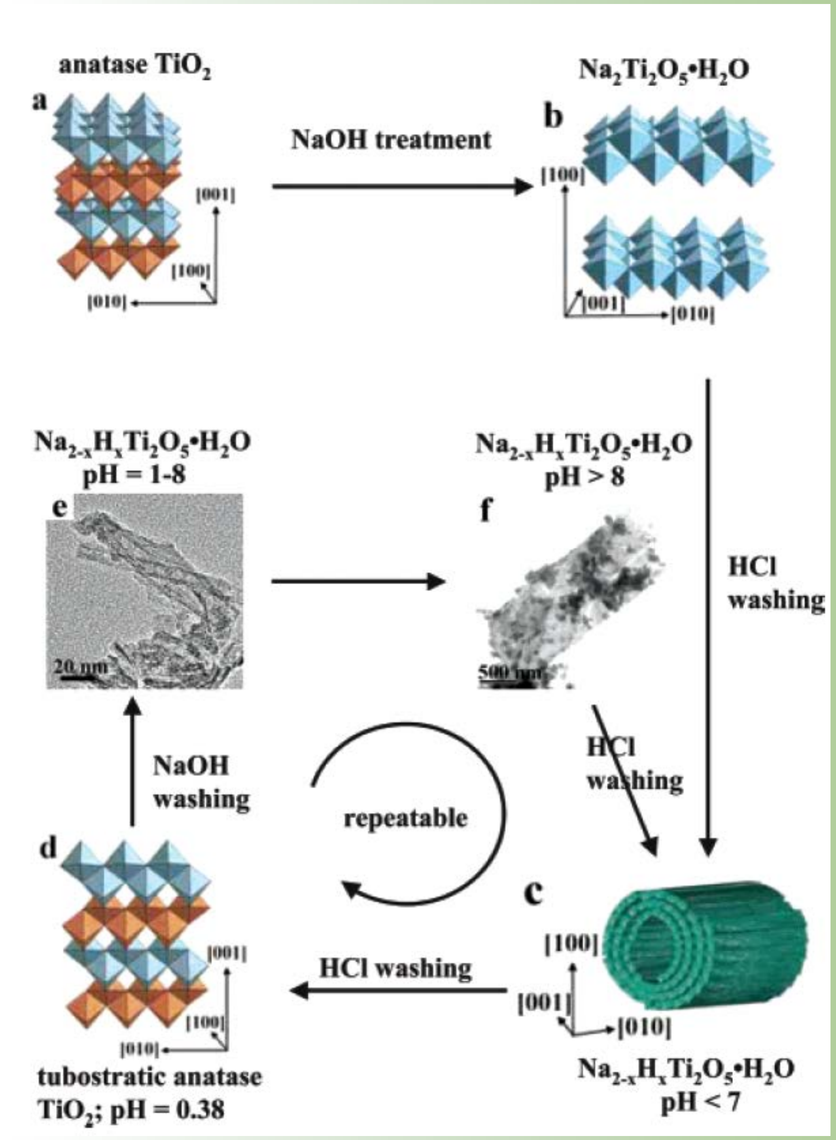
Methodology: PTNTs Preparation

- 75mL mL 10M sodium hydroxide (NaOH) solution was added to 2 grams (g) TiO_2 anatase or P25 Degussa powder and stirred for 1 hr. using a magnetic stirrer
- The slurry was added to a polytetrafluoroethylene autoclave and treated at 130°C and 140°C for 24hrs.
- The precipitate was collected (excess NaOH was removed), washed with 0.1 M hydrochloric acid (HCl) aqueous solution to a pH of 1.6 and subsequently rinsed to neutral pH with deionized water
- The neutralized precipitate was dried and ground

$$TiO_2 \text{ powder} + 10M\ NaOH \xrightarrow[130°C,\ 140°C]{\Delta} TNTs + 0.1M\ HCl + DI\ H_2O$$

$$TNTs + 0.1M\ HCl + DI\ H_2O \longrightarrow PTNTs$$

Mechanism of PTNTs Generation



*Left figure: The scheme for the formation and transformation of nanotubes generated by the NaOH hydrothermal treatment and the post-treatment washing.

- **After NaOH treatment, some Ti-O-Ti bonds are broken, some intermediates including Ti-O-Na and Ti-OH are developed.**
- **After washing with HCl above pH 8, some nano-sheets are formed.**
- **Continue washing to pH below 7, nanotubes are achieved through Na^+ exchange with H^+ in the post acid washing.**

*Chien-Cheng Tsai and Hsisheng Teng, Structural Features of Nanotubes Synthesized from NaOH Treatment on TiO2 with Different Post-Treatments, *Chem. Mater.* **2006**, *18,* 367-373

PEI-PTNTs Preparation

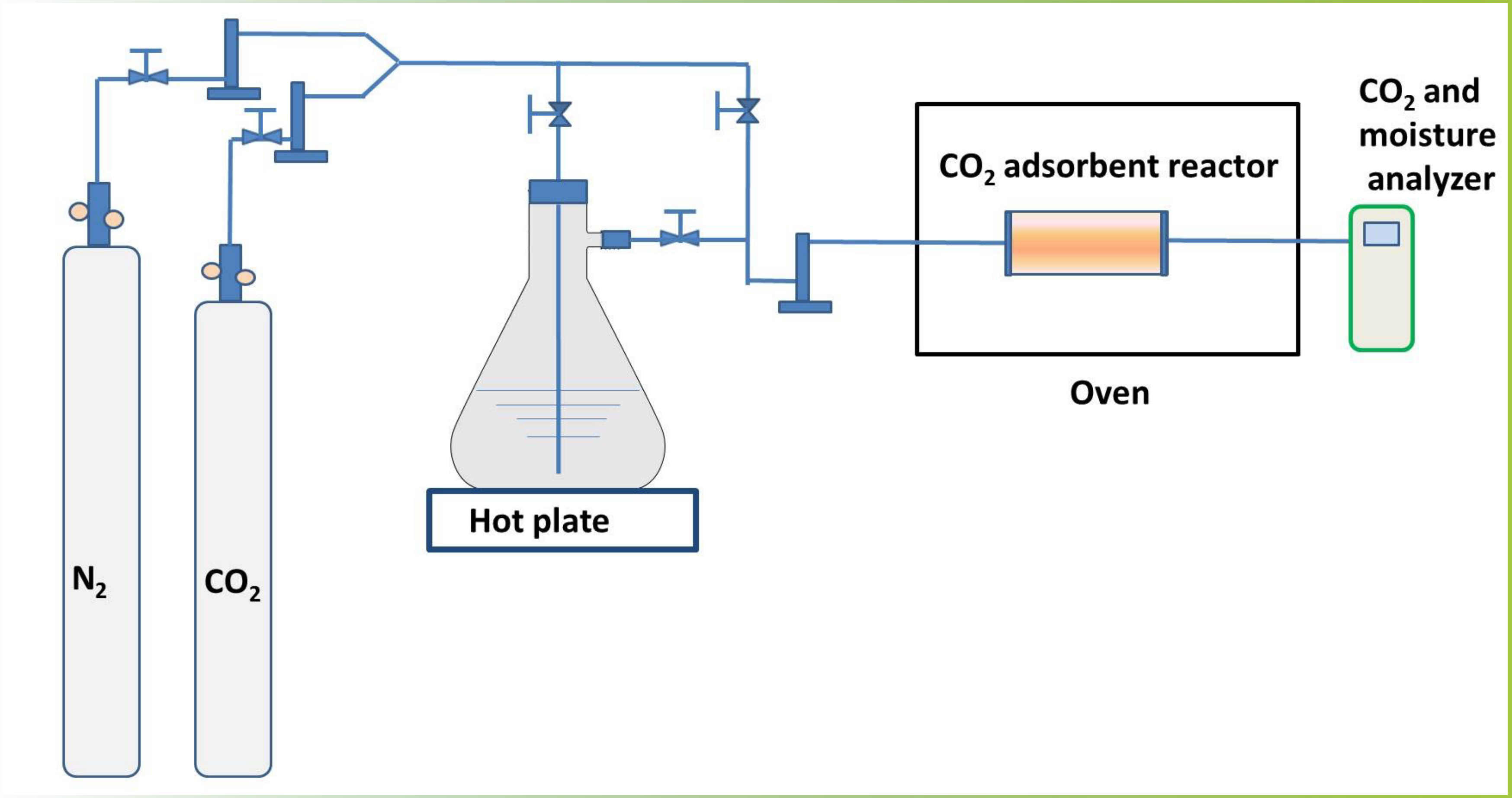
- 1 g PEI (600MW or 10,000MW) was dissolved in 20mL methanol
- 1 g PTNTs was dispersed in 60 mL methanol using a tip sonicator
- The dissolved PEI was added to the dispersed TNTs and the mixture was stirred in a covered beaker for 2 hrs. and then stirred uncovered for another 8 hrs. (to allow for wet impregnation)
- The recovered residue was dried
- The resulting product was denoted as PEI-PTNTs-50% according to the PEI loading

PEI + Methanol + PTNTs → PEI-PTNTs

Adsorption/ Desorption Cycle

- Adsorption capacity was determined using weight differential in adsorbent
- 1 g adsorbent was pretreated at 110°C with pure nitrogen (N_2) gas at 120 mL/min for 30mins. and the weight recorded
- A mixture of nitrogen and carbon dioxide (N_2/CO_2) was passed through the adsorbent at 120 mL/min flow and at 75°C for 1 hr. and the weight recorded
- The steps above were repeated and the weight differential between each set of adsorption/ desorption were calculated with the difference being regarded as the CO_2 adsorbed capacity in mg/g

Schematic of Adsorption Apparatus

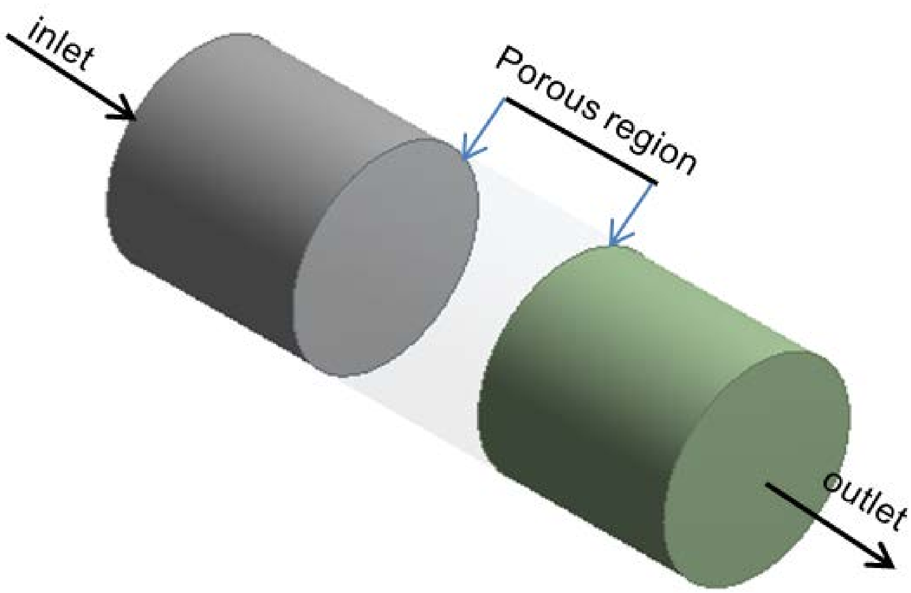


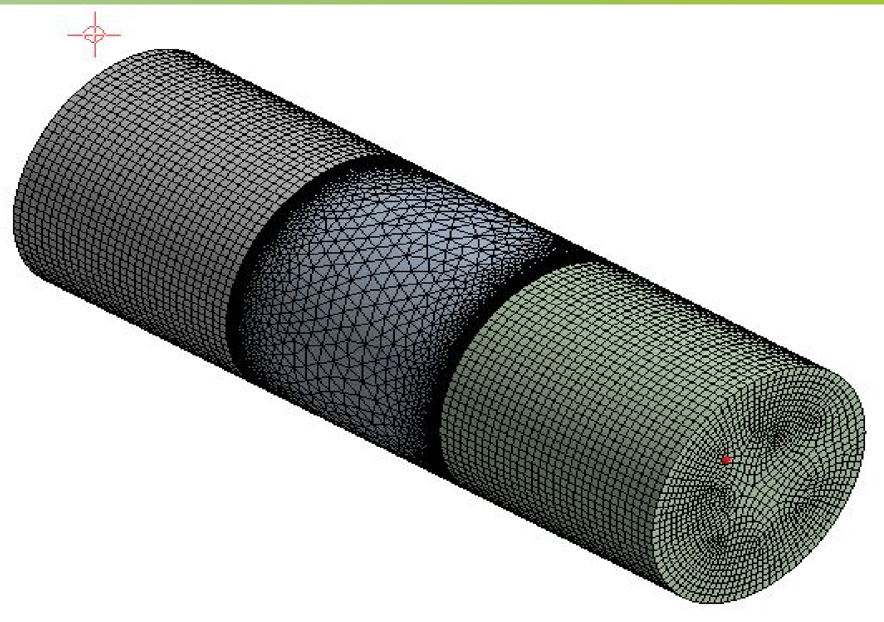
Characterization of PTNTs and PEI-PTNTs

- The crystal samples were analyzed using a Bruker D8 Advanced diffractometer with CuKα radiation and the following:
  - Scattering angle: 2θ
  - Step Size: 0.015
- JEOL 2010 transmission electron microscope (TEM)
  - Acc. voltage: 100-101
    - Start kV: 100
    - Stop kV: 200
    - Step: 10
    - Time: 15
- JEOL SEM at Department of Chemistry at Prairie View A&M University

CFD Simulations

- Simplified Geometry & Meshing of Carbon Capture Device
  - The diameter of the pipe is 1.5m
  - Approximately 2 million grids were used
  - There are 5 times finer grids in the porous domain than the two other regions



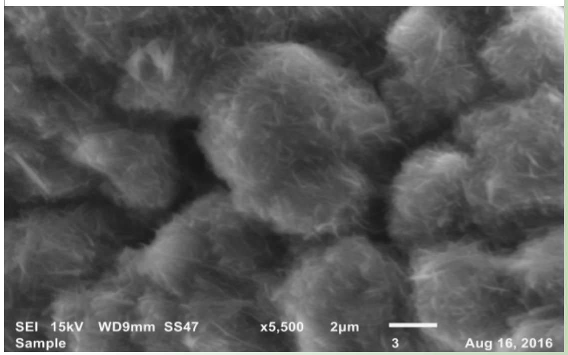


Results: Synthesis

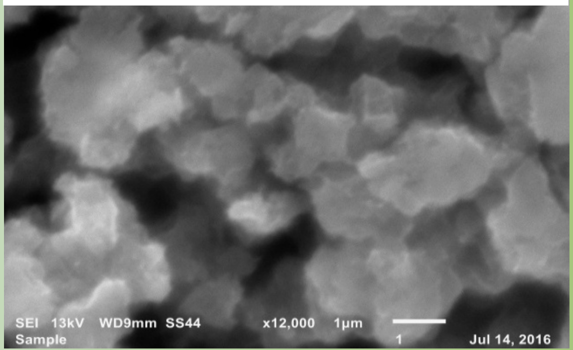
- Among the different temperatures (130-180°C), NaOH concentration (5 & 10M), HCl concentration (0.01 & 0.1) and dilute acid type (HCl & nitric acid, HNO_3)that were used, the following parameters yielded:
  - Titanate nanostructures
    - Nanosheets
    - Nanotubes
    - Nanorods

Synthesis: SEM Results

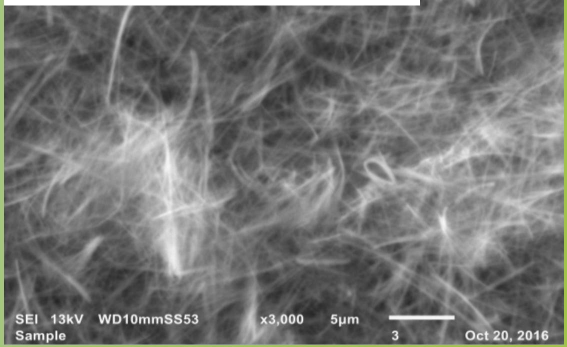
130°C 7 days 5M NaOH no wash



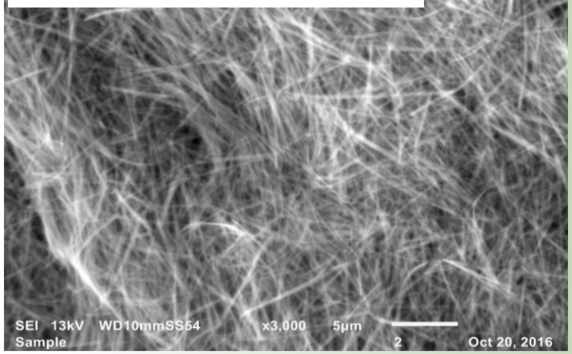
140°C 3 days alternate water/ acid wash



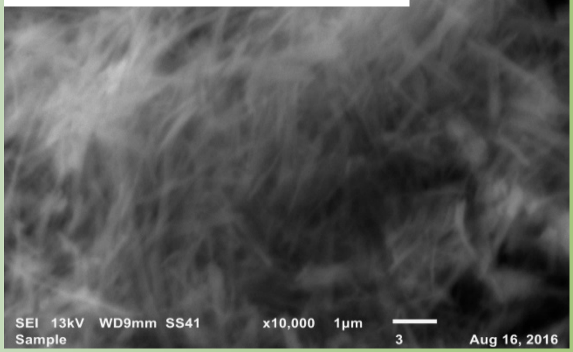
150°C 7 days water wash only



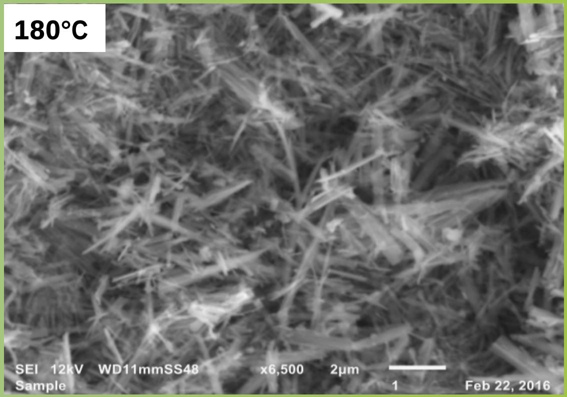
160°C 7 days water wash only



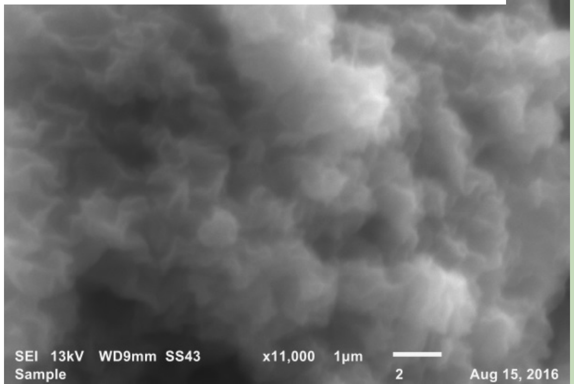
170°C 7 days water wash only



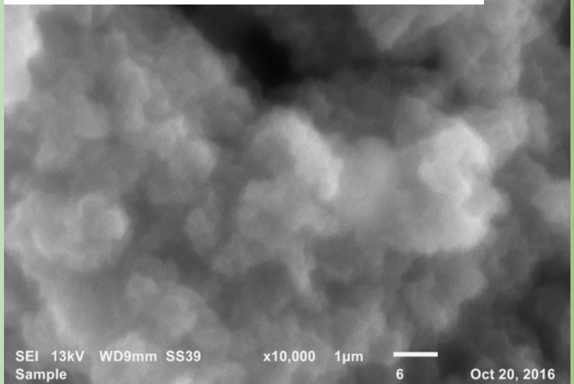
180°C



130°C 1 day HNO_3 wash (sonication)



130°C 1 day anatase 0.1M HCl wash



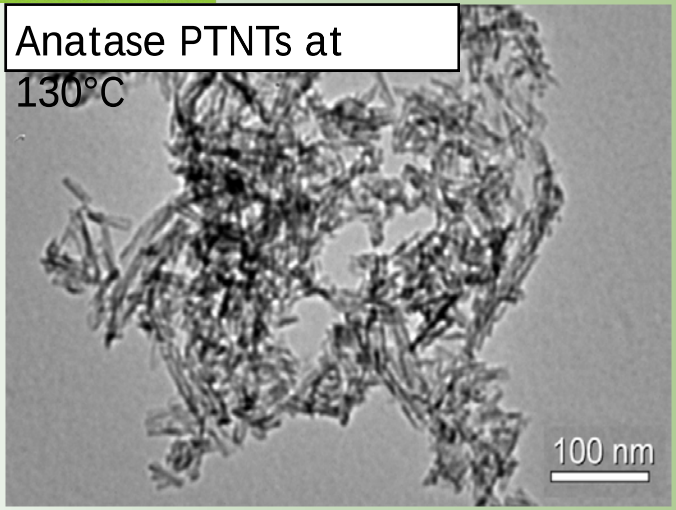
- SEM experiments showed that titanate nano-sheets were developed at 150 -180 °C.
- Titanate nanostructures obtained at 130 and 140 °C will be characterized by TEM

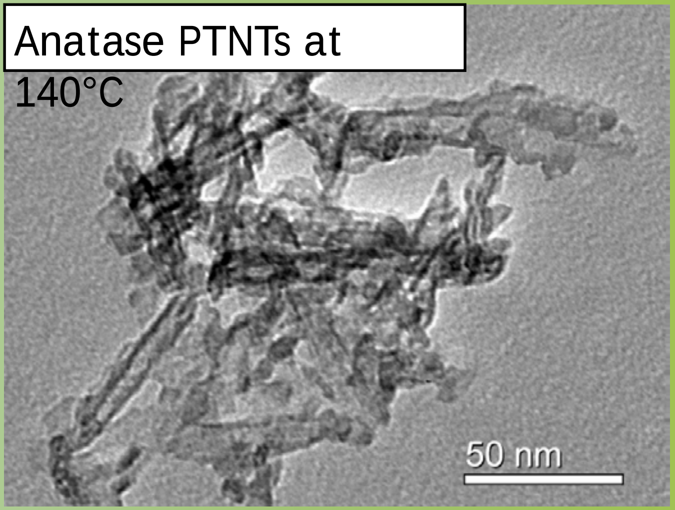
Synthesis: TEM Results

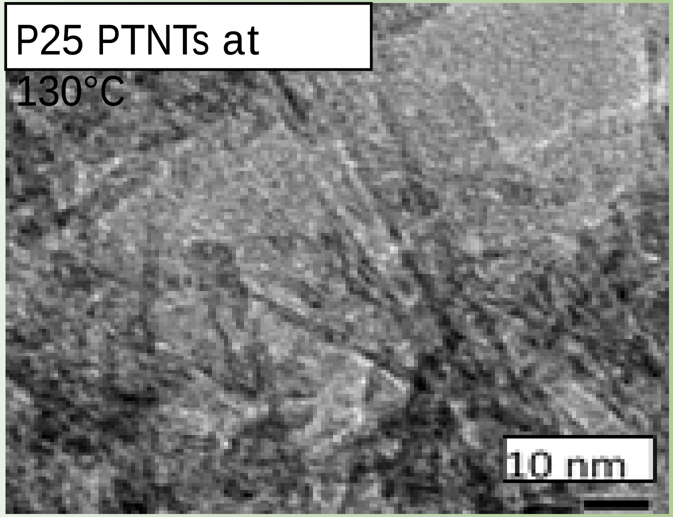
- Successful titanate nanotube formation was observed for:
  - o Anatase (130°C and 140°C - 1 day)
  - o P25 (130°C and 140°C - 1 day)

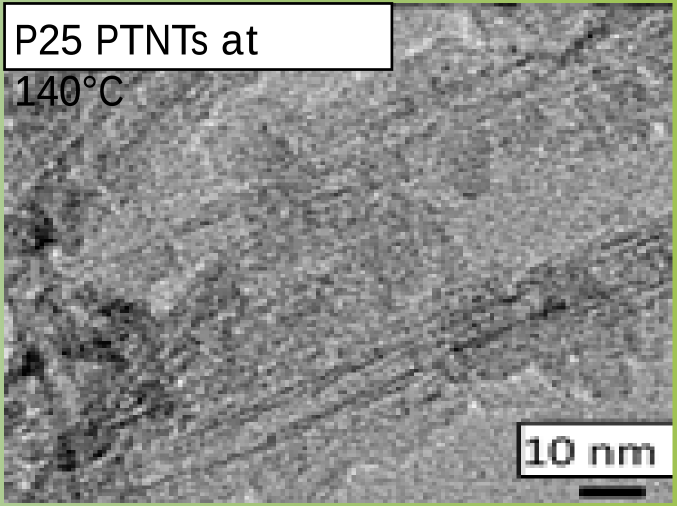
- Agglomerates of titanate nanotubes are observed for the two powders

Synthesis: TEM Results continued









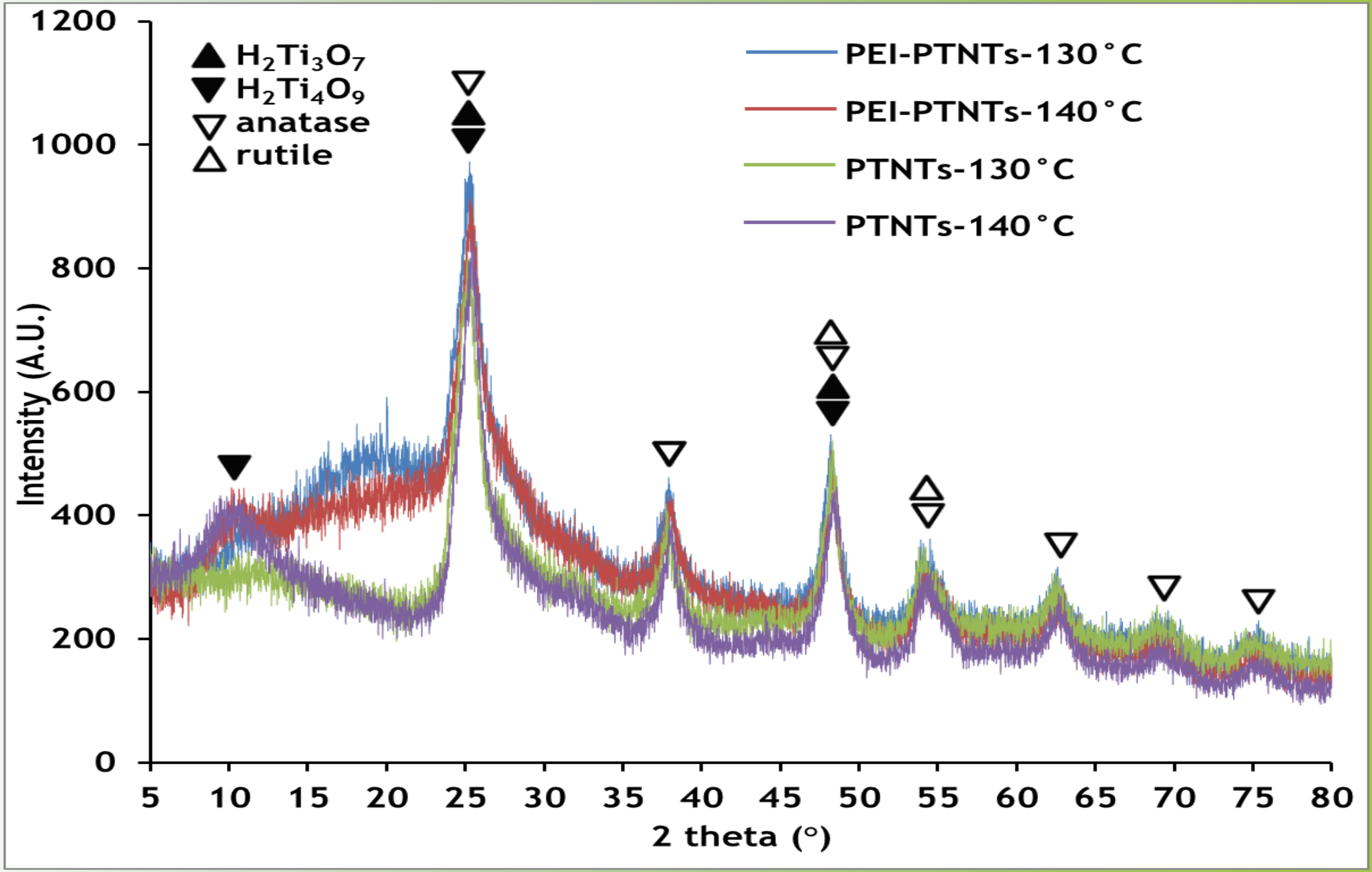
TEM characterizations demonstrated that the titanate nanotubes can be successfully developed at 130 and 140 ˚C from anatase or P25 TiO_2 nanopowder

Synthesis: XRD Results

- Powder X-ray diffraction indicate the following phases in P25 PTNTs and PEI-PTNTs
  - $H_2Ti_3O_7$
  - $H_2Ti_4O_9$
  - Anatase
  - Rutile

- These phases were consistent before and after PEI impregnation

Synthesis: XRD Results continued

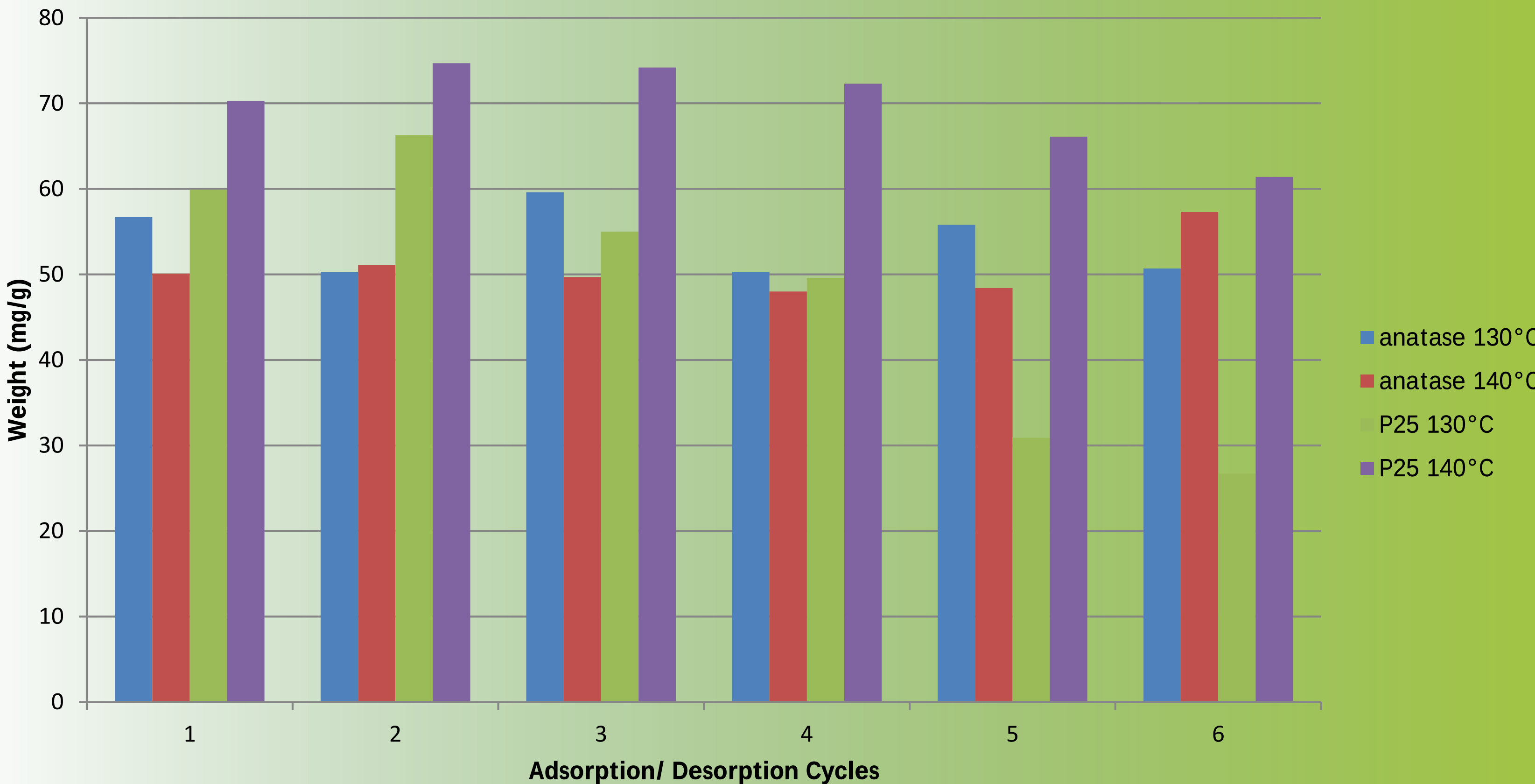


Their typical series of peaks occurs at 2θ = 9.6, 25.2, 38.0, 48.2, 62.0 degrees, representing various types of nanotubes $H_2Ti_3O_7$, $H_2Ti_4O_9$, anatase and rutile developed after hydrothermal treatment.

Adsorption Capacity

- The adsorption capacities were recorded for the following PEI-PTNTs:
  - P25 (130°C and 140°C 1 day)
  - Anatase (130°C and 140°C 1 day)
- Highest average CO_2 adsorption was with P25 140°C 1day PEI-PTNTs (69.83mg/g)
- CO_2 adsorption results are highly variable and inconclusive
- Additional experiments are planned to study this further

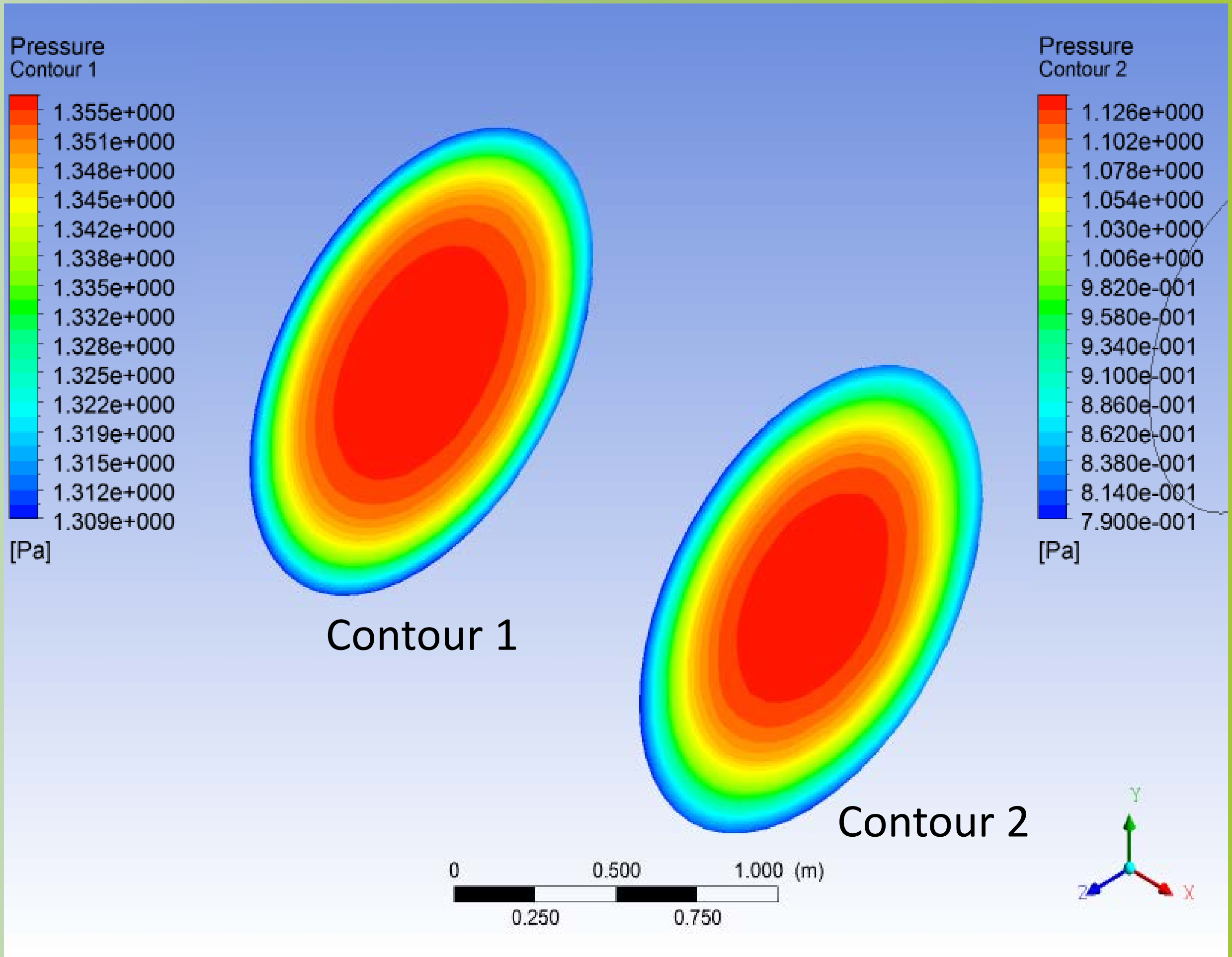
PEI-PTNTs (130°C and140°C) Adsorption Capacity (mg/g)



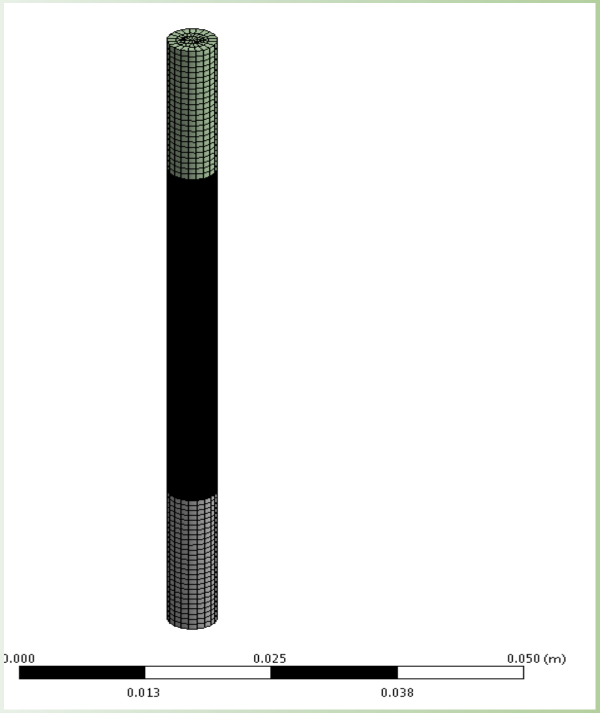
The CO_2 adsorption capacity of PEI-functionalized titanate nanotubes is influenced by raw TiO_2 material for synthesis of titanate nanotubes, gas flow rate, adsorption temperature, CO_2 concentration and pressure.

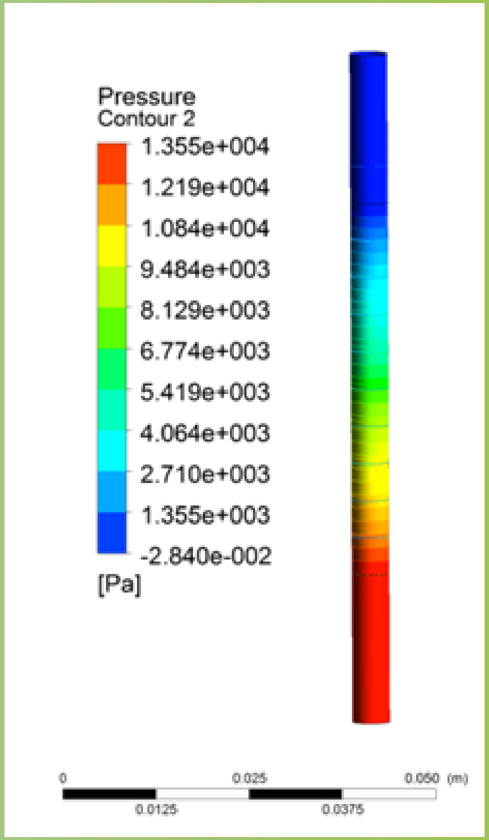
CFD Simulation of CO_2 Capture

- The pressure contour is for a case of 50% porosity
- Contour 1&2 represents before entering and after exiting the porous region
- Pressure drops at the exit of the porous region



CFD Simulation of CO_2 Capture in a Vertical Pipe





- Vertical flow pipe
- Grids in the porous region are made finer than the top and bottom portions of the pipe to achieve better results
- The flow rate is 250 cm^3/min
- The size of the particles used is 250μm

Conclusions

- TEM characterized scattered and overlapped PTNTs as tubular nanostructures for 130°C and 140°C (anatase and P25 powders)
- TEM images confirmed both ends of the nanotubes are open for P25 nanotubes.
- No remarkable peak shift occurred before or after PEI impregnation as confirmed with XRD characterizations
- CO_2 adsorption from the simulated flue gas was observed using PEI-functionalized titanate nanotubes synthesized from anatase and P25 TiO_2 nanopowder at 130 and 140 ºC; however, adsorption capacities are highly variable and inconclusive
- CFD simulations were used to produce the pressure contours to simulate our experimental conditions and increased pressure was observed at the inlet of CO_2 gas in a vertical flow pipe

Future Studies

- Develop other PEI varied adsorbents using different molecular weights of PEI
- Optimize the adsorption/ desorption cycle procedures
- Determine surface area measurements of the varied adsorbents
- Optimize CFD simulations with experimental parameters

Emerging Researchers National Conference in STEM 2016

- For her work done with this research project, Melisa Stewart was awarded:
  - **1st place** in Ecology, Environmental and Earth Sciences in graduate oral presentations

Acknowledgements

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- Some of the personnel are supported through The National Science Foundation (NSF) through the Center for Energy and Environmental Sustainability (CEES) a NSF CREST Center, Award #1036593

- The Investigators would like to thank:
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  - Texas A&M Microscopy & Imaging Center
  - Dr. Hylton McWhinney and Mr. Tony Grady; Department of Chemistry, Prairie View A&M University

Questions?