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

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Outline

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- Conclusions
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Post Combustion Capture Technologies

- Carbon Capture: Pre-combustion, oxy-combustion, and post-combustion
- Amine absorption
- Solid adsorbents
  - Activated carbon
  - Zeolites
  - Silica materials
  - Metal organic frameworks (MOFs)
  - Amine-modified adsorbents
    - Monoethanolamine (MEA) and diethanolamine (DEA)
    - triethylamine (TEA), tetraethylenepentamine (TEPA) and triethylenetetramine (TETA)
    - Polyethylenimine (PEI)

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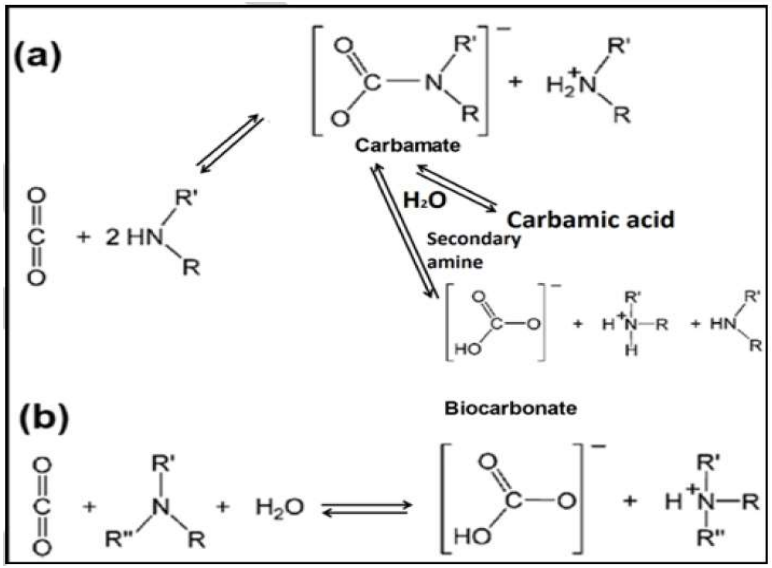
Reaction mechanisms of Amines with CO_2

- Reactions between primary and secondary amines with CO_2 produces
  - Zwitterion -> carbamate (dry conditions)
  - Carbamic acid, carbonate and bicarbonate in presence of water
- Reaction of tertiary amines produces bicarbonate in the presence of water



Shen et al. Energy Technol. 2017, 5, 822 – 833

Polyethylenimine (PEI)

- A polymer composed of repeating units that contain one amine group
- PEI occurs in three types:
  - Linear PEI fragments that contains all secondary amines
  - Branched PEI fragments (used in this study) contains primary, secondary and tertiary amines in the ratio 30:40:~30
  - Dendrimer PEI has only primary and secondary amines
- Some advantages of PEI compared to other amines such as MEA are:
  - PEI is more thermostable
  - Easily synthesized
  - Is relatively cheap
- PEI can be loaded onto supports through
  - Copolymerization
  - Impregnation
  - direct condensation
  - post-synthesis grafting

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Protonated Titanate Nanotubes (PTNTs)

- PTNTs are TiO_2 derived nanotubes that have been protonated using acid
- It has been used in many applications such as catalyst supports, UV absorbers, photocatalysts and now CO_2 capture
- It is attractive for CO_2 capture due its precursor TiO_2 powder being relatively cheap and nanotubes have large specific surface area and unique shape that allow for functionalization
- It can be synthesized by sol-gel method, electrochemical anodic oxidation method, assisted templated method and **hydrothermal method**
  - The simplest and cheapest of these methods is the hydrothermal method

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Objectives

- Develop a novel amine functionalized nanomaterial of protonated titanate nanotubes functionalized with polyethylenimine (PEI) to efficiently capture CO_2 from the flue gas in fossil energy power generation
  1. Establish knowledge on protonated titanate nanotube (PTNTs) synthesis
  2. Develop optimized protocols for PTNTs synthesis and impregnation of PTNTs with PEI
  3. Characterize the impregnated nanotubes and use them for refining synthesis parameters such as temperature, time and concentration
  4. Investigate the efficiency of impregnated PTNTs for capture of CO_2

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Methodology: Synthesis of Protonated Titanate Nanotubes

PTNTs were prepared using modified hydrothermal treatment methods as described in the literature

1. **Hydrothermal Treatment (three starting materials: anatase, rutile and P25 Degussa TiO_2 powders)**
   - 75mL mL 10 N sodium hydroxide (NaOH) solution was added to 2 grams (g) TiO_2 powder and stirred for 1 h using a magnetic stirrer
   - The slurry was added to a Teflon lined stainless steel autoclave and treated at 120°C -150°C for 1 – 5 days
2. **Protonating titanate nanotubes through washing process**
   - The room temperature cooled precipitate was collected (excess NaOH was removed), washed with 0.1 M hydrochloric acid (HCl) aqueous solution to pH less than 2 and subsequently rinsed to pH = 7 with deionized water
   - The neutralized precipitate was dried in an oven at 100 ° C and ground in preparation for PEI impregnation
   - The final products of protonated titanate nanotubes (PTNTs) were denoted as 130 or 140 ° C PTNTs 1 day and 130 or 140 ° C PTNTs 3 days

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

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

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Preparation of PEI Functionalized PTNTs

A wet impregnation method was used to prepare the PEI functionalized PTNTs with 50 wt % PEI

- 1 g PEI was dissolved in 25 mL 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 h and then stirred uncovered for an additional 8 h
- The recovered residue was dried in an oven at 75°C
- The final products of PEI-PTNTs were denoted as 130 or 140°C PEI-PTNTs 1 day and 130 or 140°C PEI-PTNTs 3 days

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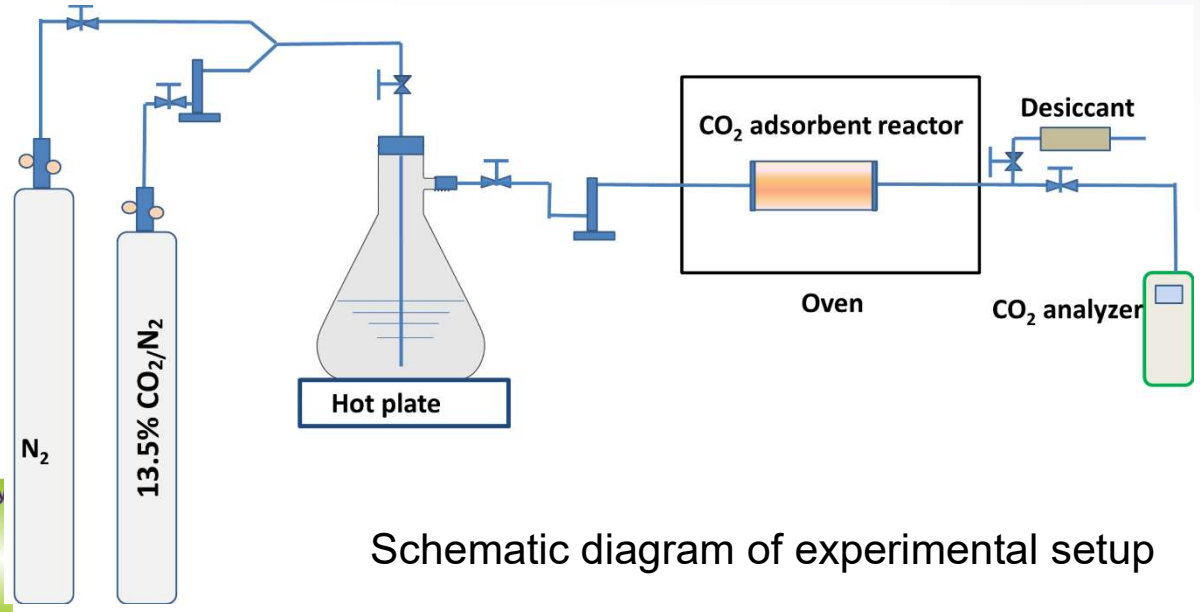
Characterization of Materials

- Transmission electron microscope (TEM): JEOL JEM-2010 TEM
- Powder X-ray diffraction: The crystal samples were analyzed using a Bruker D8 Advanced X-ray diffractometer with CuKα radiation and the following:
  - Scattering angle: 2θ
  - Step Size: 0.015
- Scanning electron microscope (SEM): JEOL JSM-6010LA SEM
- Surface area and porosity analysis:
  - Quantachrome NOVA 4200e Surface & Pore Analyzers
- Fourier-transform infrared (FTIR) spectroscopy
  - IR-200Thermo-Nicolet 2.2 (KBr) was used to confirm the presence of functional groups
- Thermogravimetric analysis (TGA)
  - TGA Q500 (TA Instrument, Inc.)

CO_2 Adsorption and Desorption Measurements

Adsorption capacity was determined using weight differential in adsorbent

- 0.5 g PEI-PTNTs adsorbent was pretreated at 110°C with pure nitrogen (N_2) gas at 120 mL/min for 60min and the weight recorded
- A mixture of nitrogen and carbon dioxide (13.5% CO_2/N_2) was passed through the adsorbent at 120 mL/min flow and at 75°C for between 60 -90 min 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 diagram of experimental setup

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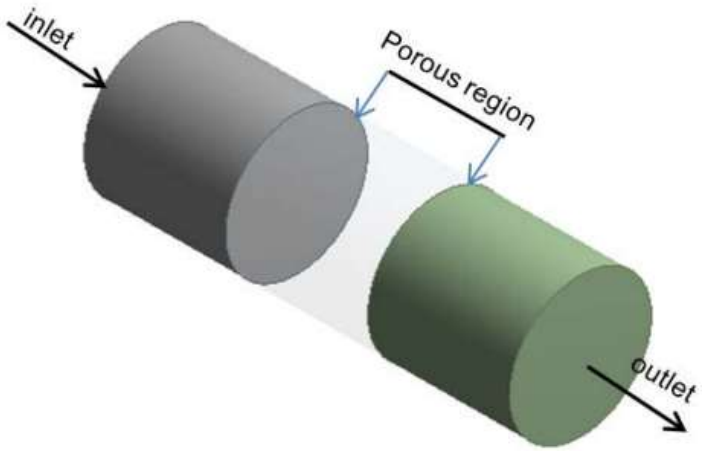
CFD Simulations

- 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



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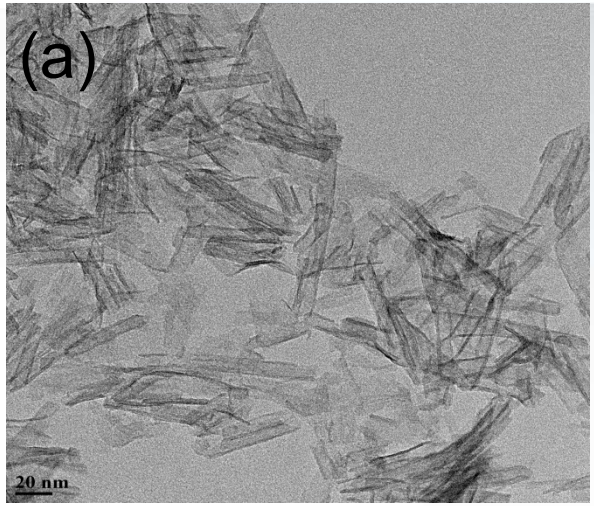
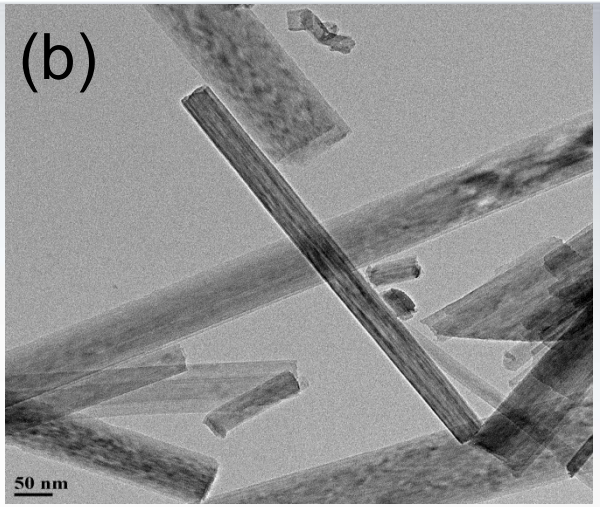
RESULTS & DISCUSSION

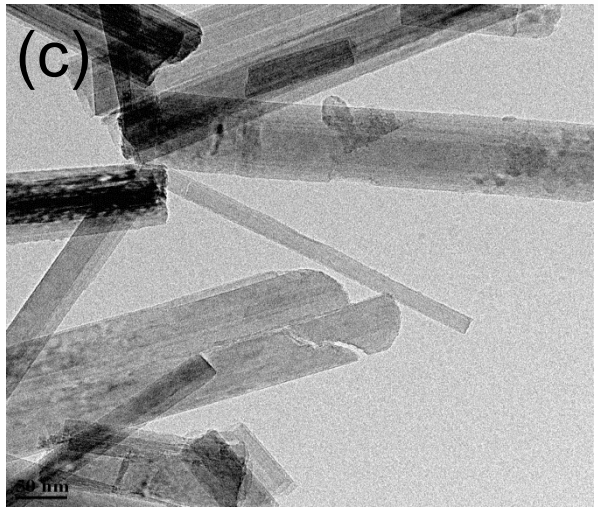
Effect of Hydrothermal Treatment Time and Temperature

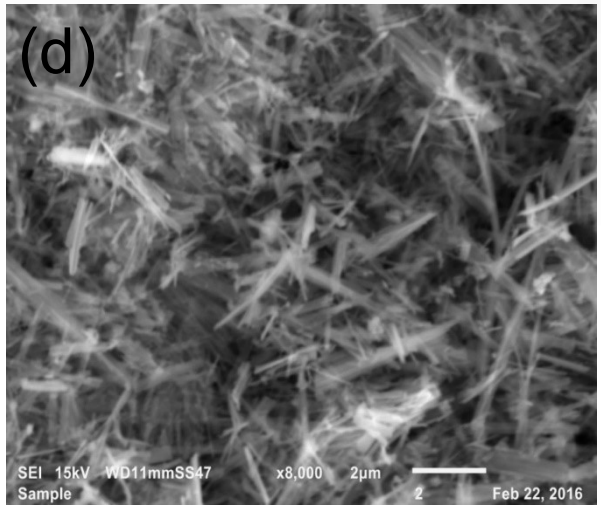
- Hydrothermal synthesis was conducted on
  - P25 Degussa TiO_2 powders, anatase, rutile
  - Time for synthesis was 1-7 days
  - Temperature range 120-180°C
  - To attain protonate titanate nanotubes, hydrothermally synthesized nanotubes were washed with 0.1 M HCl to pH less than 2 followed by DI water wash to pH of 7

Hydrothermal Synthesis of P25 Degussa TiO_2 powder









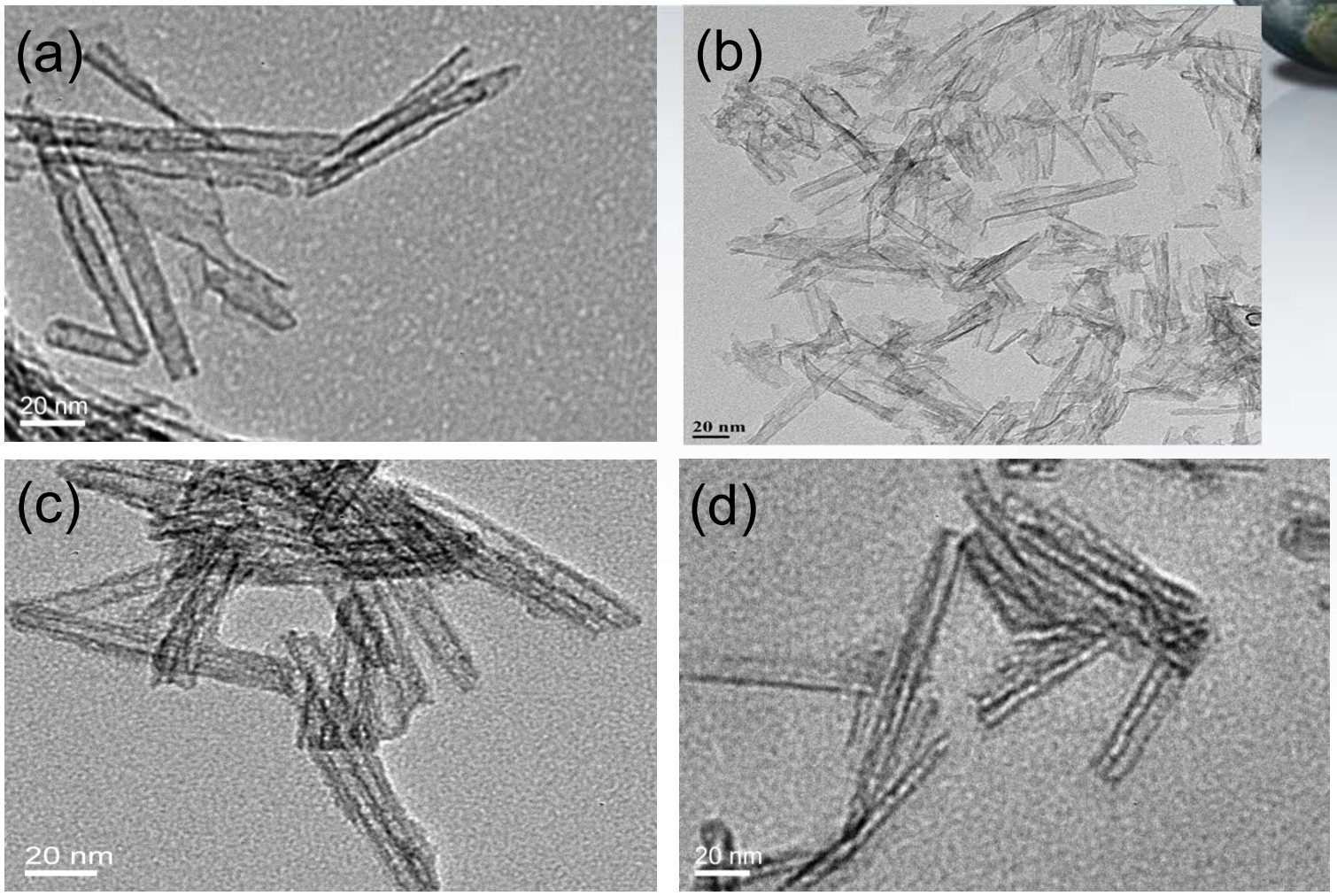
(a) P25 140°C-PTNTs-7 days

(b) P25 150°C-titanate nanofibers-7 days

(c) P25 170°C-titanate nanofibers-7 days

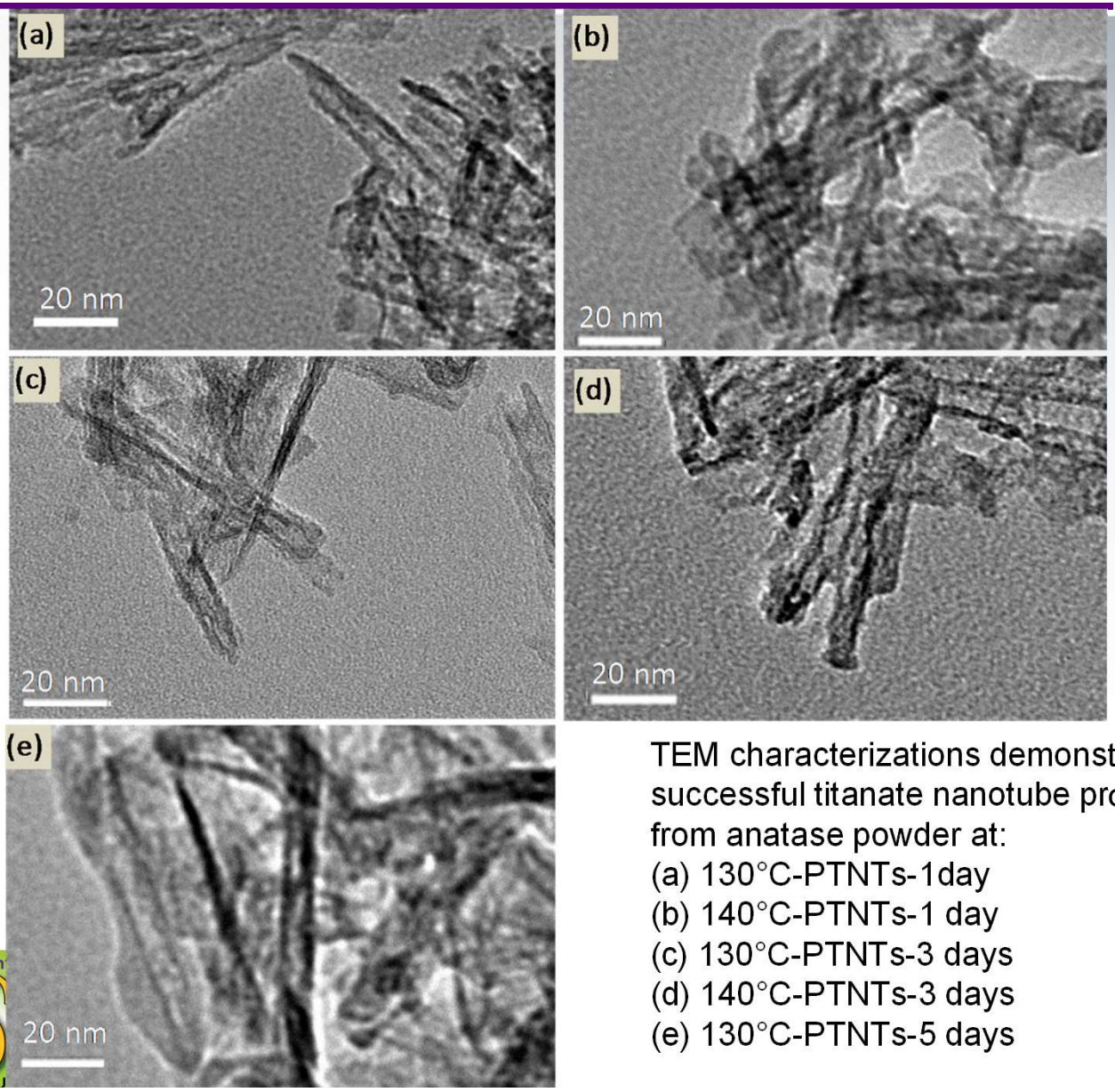
(d) P25 180°C-titanate nanofibers 7 days

Hydrothermal Synthesis of P25 Degussa and rutile TiO_2 powders



(a) rutile 120°C-PTNTs-1day; (b) P25 130°C-PTNTs-1 day
(c) rutile 120°C-PTNTs-3 days; (d) rutile 150°C-PTNTs-1 day

Hydrothermal Synthesis of Anatase PTNTs



TEM characterizations demonstrated successful titanate nanotube production from anatase powder at:
(a) 130°C-PTNTs-1day
(b) 140°C-PTNTs-1 day
(c) 130°C-PTNTs-3 days
(d) 140°C-PTNTs-3 days
(e) 130°C-PTNTs-5 days

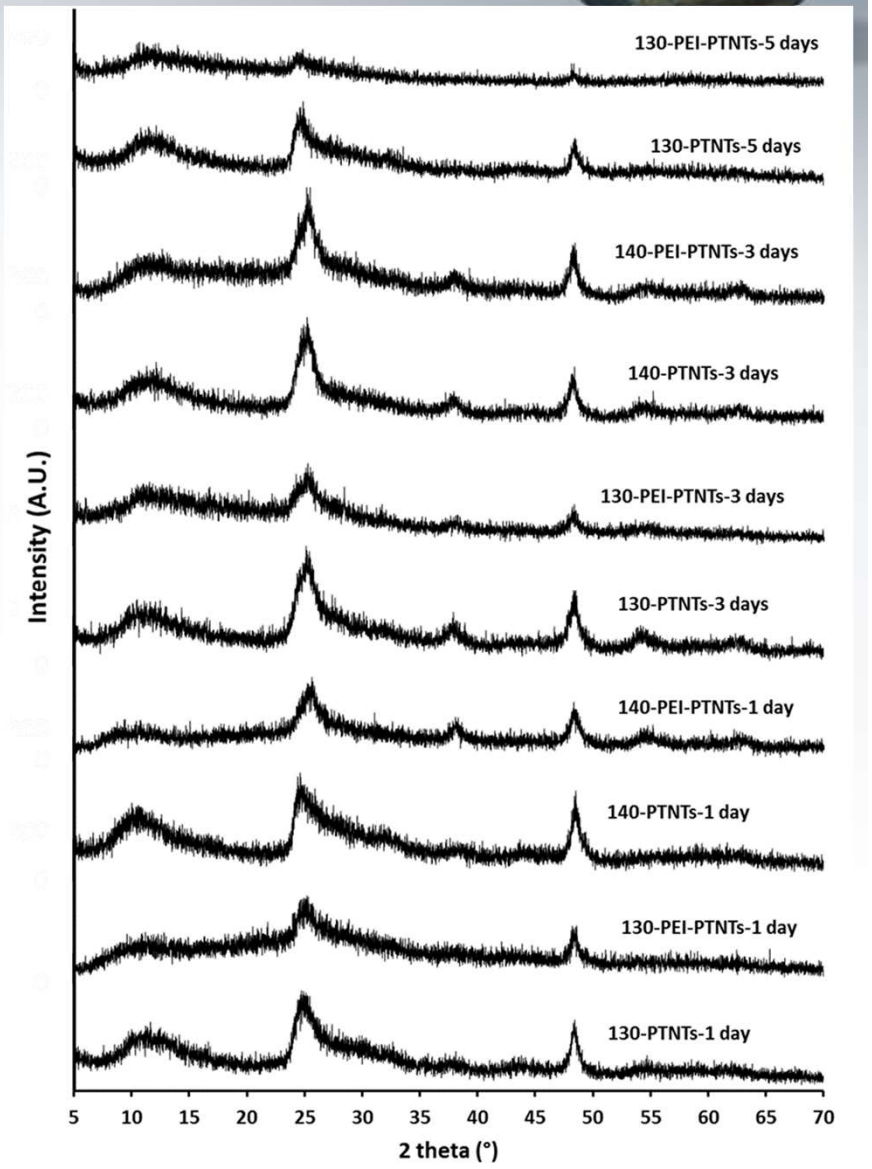
Surface Area and Porosity Analysis

- Specific surface areas (SSAs)
  - 130°C-PTNTs-3 days < 130°C-PTNTs-1 day <140°C-PTNTs-1 day < 140°C-PTNTs-3 days<130°C-PTNTs-5 days
- Pore volume
  - 140°C-PTNTs-1 day < 130°C-PTNTs-3 days < 130°C-PTNTs-1 day < 140°C-PTNTs-3 days<130°C-PTNTs-5 days
- Pore diameter
  - 140°C-PTNTs-1 day < 140°C-PTNTs-3 days < 130°C-PTNTs-5 days <130°C-PTNTs-3 days < 130°C-PTNTs-1 day

Sample	Surface area (BET), m^2/g	Pore volume, cm^3/g	Pore diameter (BJH), nm
130°C-PTNTs-1 day	314.4	1.177	15.320
140°C-PTNTs-1 day	350.5	1.000	14.342
130°C-PTNTs-3 days	309.9	1.109	14.918
140°C-PTNTs-3 days	351.7	1.221	14.344
130°C-PTNTs-5 days	403.4	1.447	14.836

XRD Patterns of Anatase PTNTs

- XRD patterns of the PTNTs and PEI-PTNTs
- Similarity in peak positions for all samples before and after the loading
- Weakened by loading PEI onto/into the nanotubes



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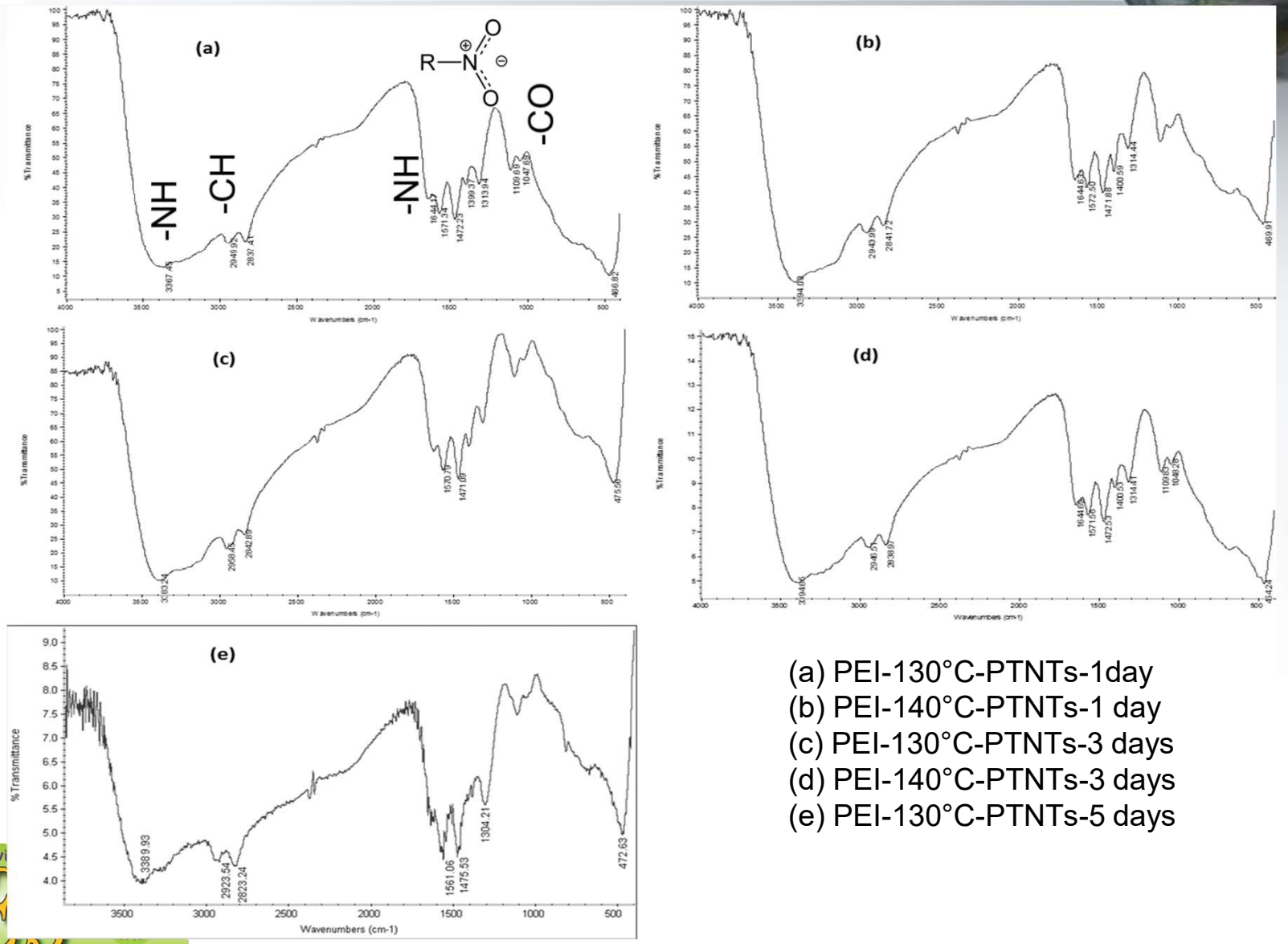
FTIR spectra of PEI-PTNTs



(a) PEI-130°C-PTNTs-1day
(b) PEI-140°C-PTNTs-1 day
(c) PEI-130°C-PTNTs-3 days
(d) PEI-140°C-PTNTs-3 days
(e) PEI-130°C-PTNTs-5 days

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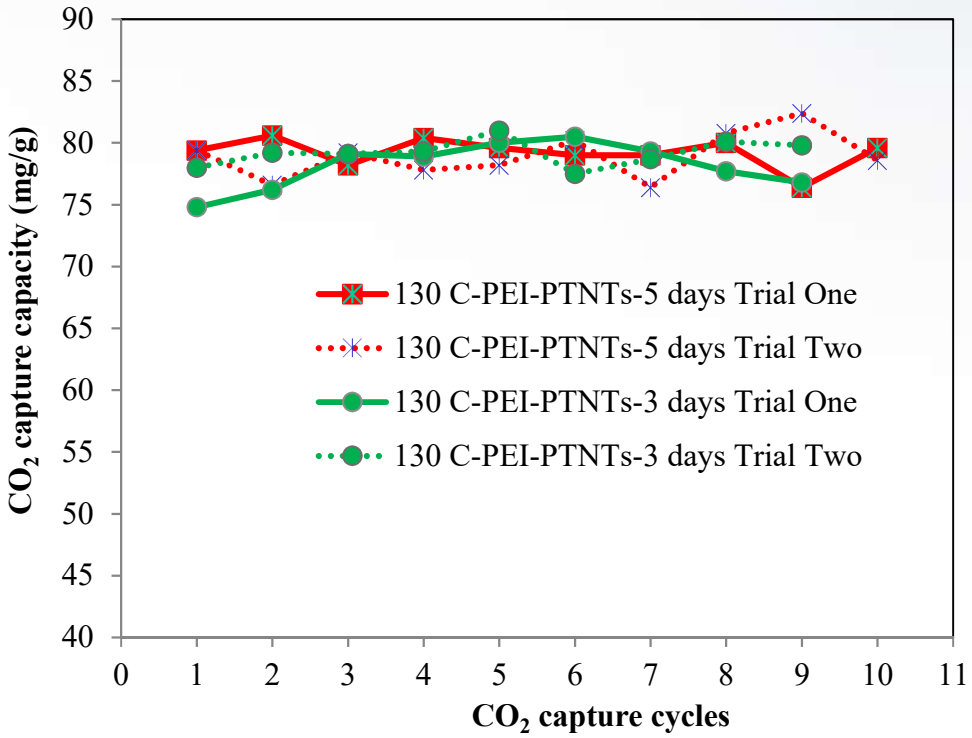
Adsorption Capacities of Anatase PEI-130°C-PTNTs-3, 5 days

- Anatase PEI-PTNTs produced within 3 and 5 days hydrothermal synthesis displays similar adsorption/ desorption cyclic pattern
- Average adsorption capacities were 79.2 and 79.0 mg/g for 130°C-PEI-PTNTs-5 days and 130°C-PEI-PTNTs-3 days, respectively



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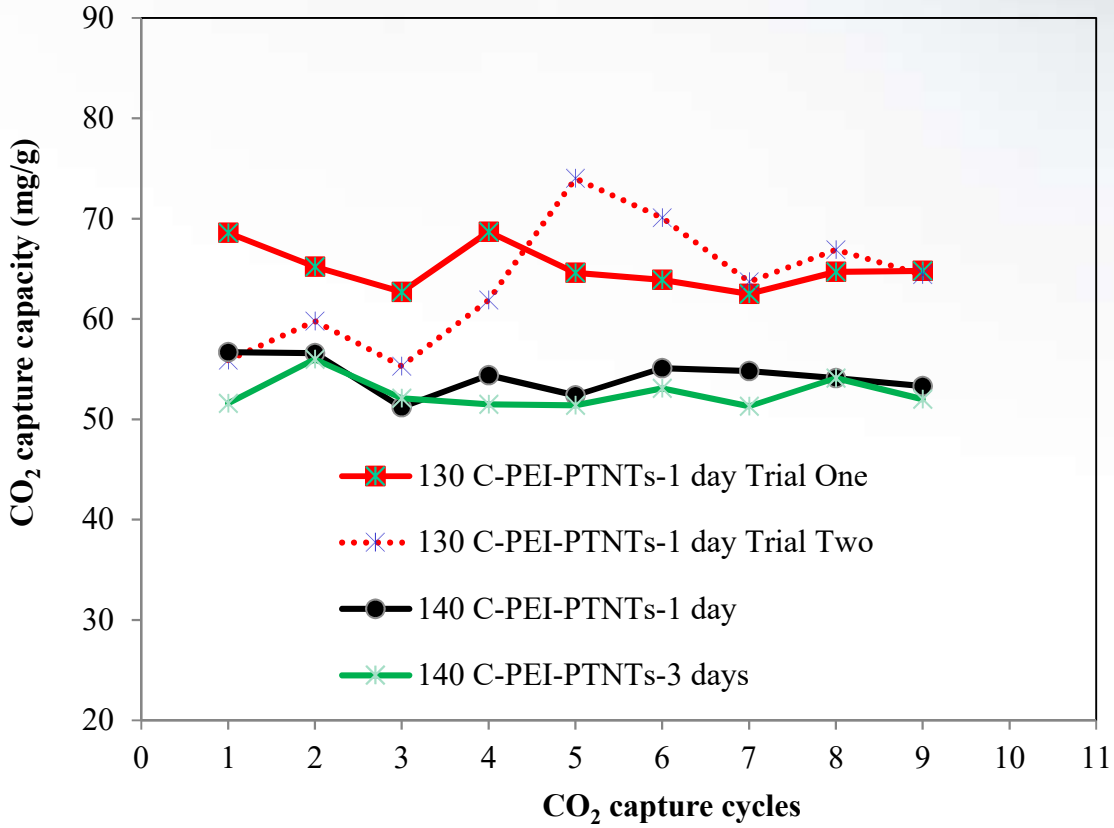
Adsorption Capacities of Anatase PEI-PTNTs-1,3 days

- Lowest Capture capacity of 140°C PEI-PTNTs
- Average adsorption capacities of two trials were 64.8 and 64.4 mg/g for 130°C-PEI-PTNTs-1 day, respectively



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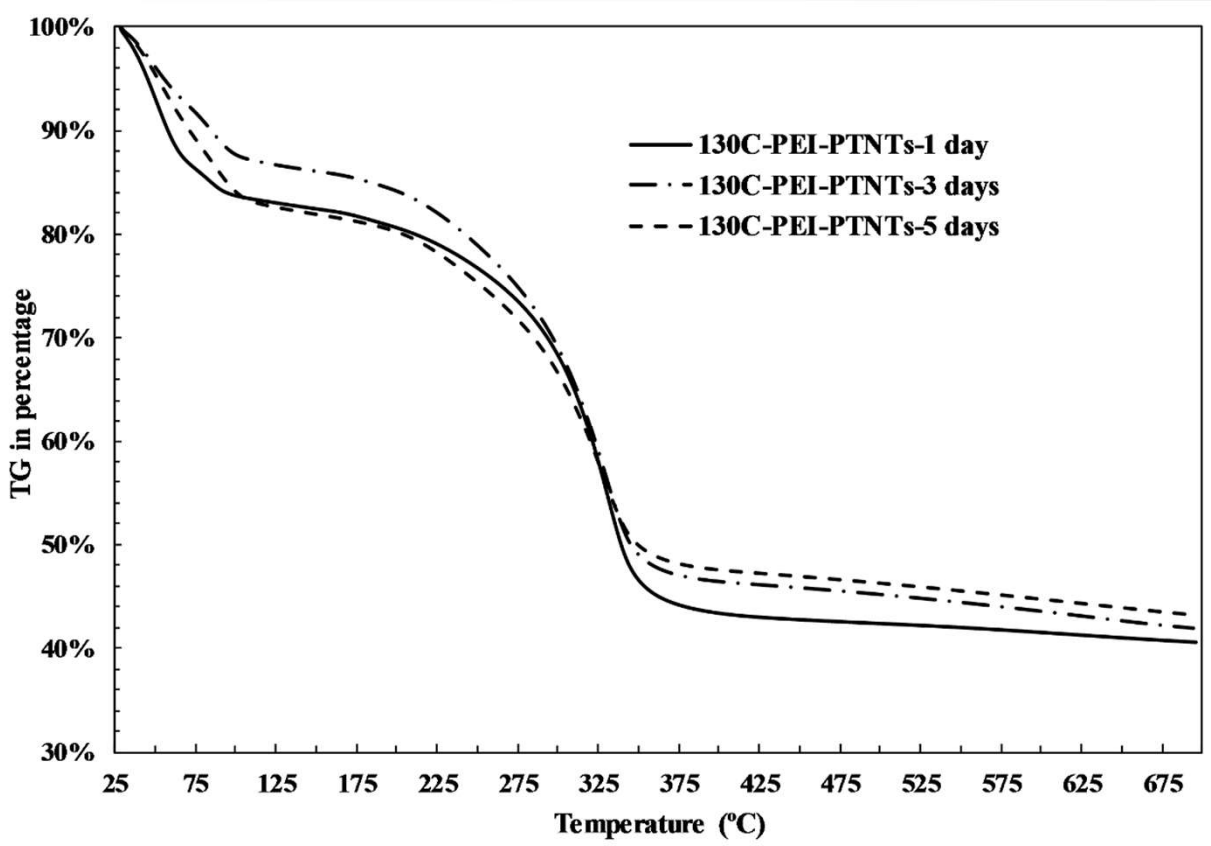
Thermal Stability of the Fabricated Adsorbents

- Three specimens synthesized at 130°C
- Mass loss in four stages
- Similarity in thermal stability



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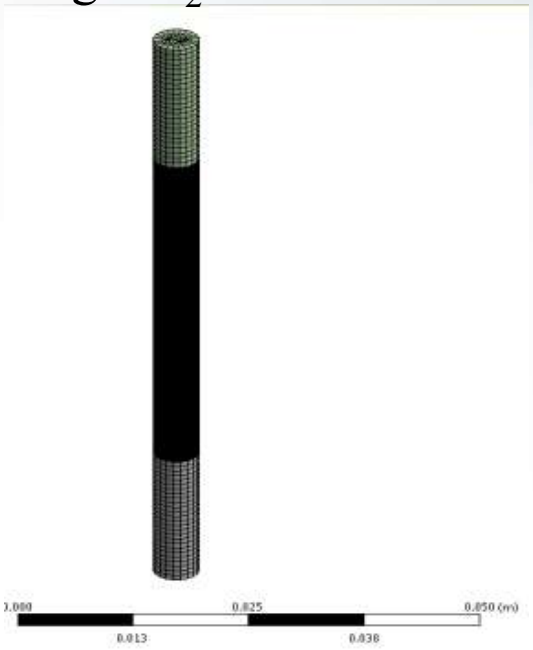
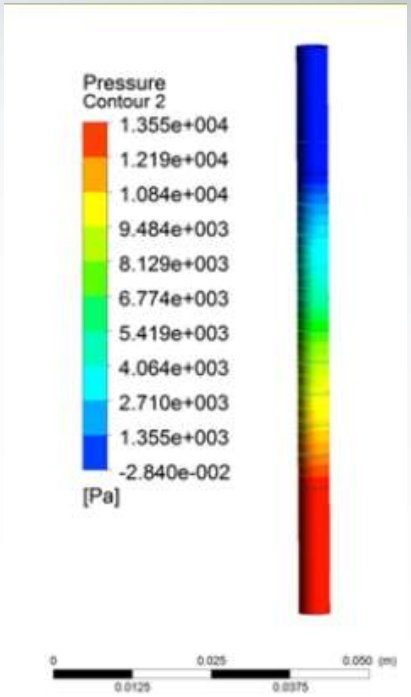
CFD Simulation of CO_2 Capture in a Vertical Pipe

Purpose: Initialize the design of a carbon capture system scrubbing CO_2 with PEI-PTNTs

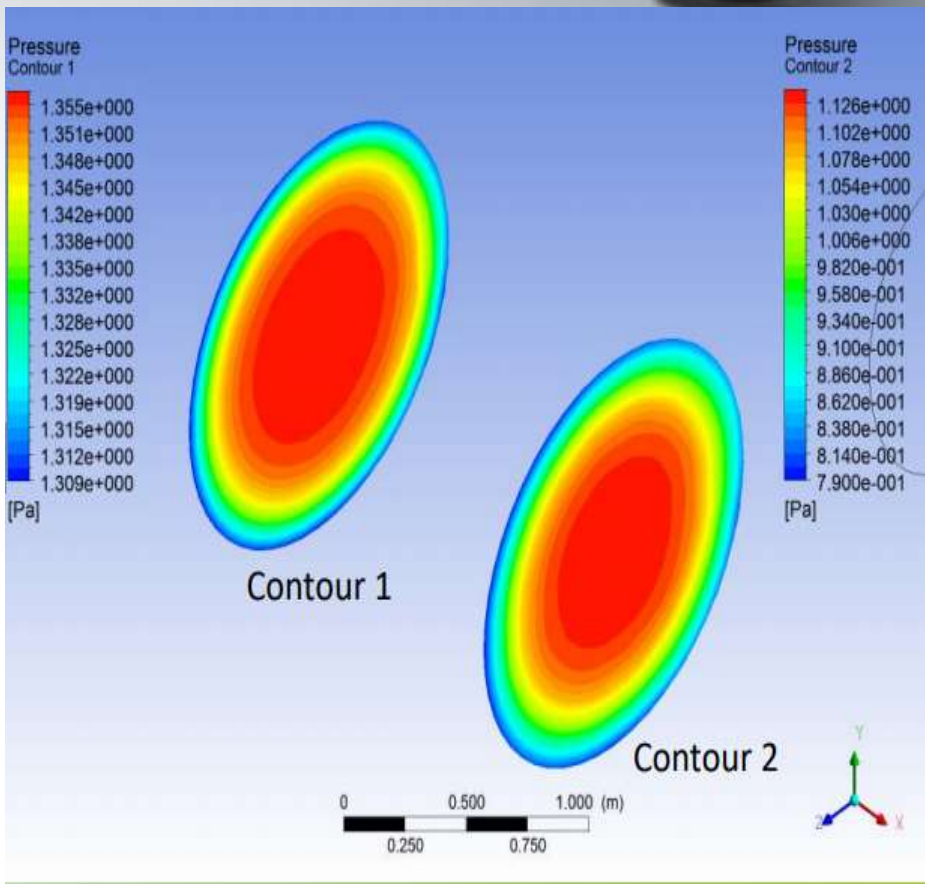




- Vertical flow pipe
- Grids in the porous region are made finer than the top and bottom portions of the pipe to achieve better results
- The flow rate is 250 cm^3/min
- The size of the particles used is 250μm

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



Conclusions

1. PTNTs can be produced by hydrothermal synthesis of anatase, rutile and P25 Degussa TiO_2 powders at 120-150°C
2. Optimal PTNTs production can be achieved by hydrothermal synthesis at 130°C followed by dilute HCl wash and DI water wash
3. XRD confirms PEI impregnation does not affect PTNTs structure as no noticeable peak shifts are observed
4. Hydrothermal synthesis conditions affect physical properties of PTNTs, such as surface area, pore volume and pore diameter
5. The surface area, pore volume and pore diameter of PTNTs influence the carbon capture capacity
6. Optimal CO_2 capture was achieved using 130°C-PEI-PTNTS-3 days

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Project Outcomes

- Two peer-reviewed journal papers
  - Xinhua Shen, Hongbo Du, Riley H. Mullins, and Raghava R. Kommalapati. "Polyethylenimine Applications in CO_2 Capture and Separation: from Theoretical Study to Experimental work." Energy Technology 5, no. 6 (2017), 822-833.
  - Hongbo Du, Melisa L. Stewart, Xinhua Shen, Raghava R. Kommalapati. “The Effects of Synthesis Conditions on the Carbon Capture Capacity of Polyethylenimine Impregnated Protonated Titanate Nanotubes” submitted to Environmental Technology.
- Two graduate, four undergraduate and one high school students were trained in the project.
- Four presentations at national conferences.
  - A gradate student won the first place of oral presentation in the 2016 Emerging Researchers National (ERN) Conference in STEM
- Four presentations at local/regional conferences

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Questions?