NOVEL SILICA NANOSTRUCTURED PLATFORMS WITH ENGINEERED SURFACE FUNCTIONALITY AND SPHERICAL MORPHOLOGY FOR LOW-COST HIGH-EFFICIENCY CARBON CAPTURE (FE-0023541)

– *KICK-OFF PRESENTATION* –

Cheng-Yu Lai , Daniela Radu
Delaware State University

HBCU/UCR Kick-Off Meeting
Morgantown, West Virginia, October 27-28, 2014
National Energy Technology Laboratory

Outline

- The Project Team
- Technical background / motivation for the project
- Potential significance of the results of the work
- Relevancy to Fossil Energy
- Statement of Project Objectives (SOPO)
- Project milestones, budget, and schedules as related to SOPO tasks
- Project risks and risk management plan
- Other relevant aspects of the project management plan (PMP)
- Project status

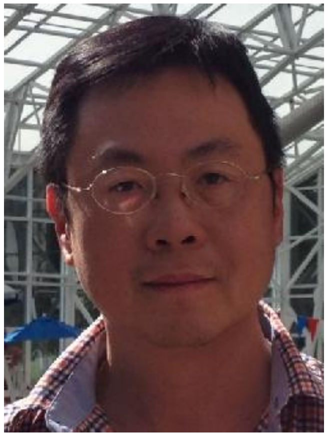
The Project Team

PI – Cheng-Yu Lai

Co-PI – Daniela Radu

One graduate student – to be hired

The Project Team



PI Dr. Cheng-Yu Lai - Associate Professor (tenure-track), Department of Chemistry at Delaware State University (since 2012).

Prior experience:

- Senior researcher at DuPont CR&D, Wilmington, DE - coordinated activities related to ***synthesis and application of novel battery materials based on mesoporous carbon-sulfur as cathode for Li-ion batteries***.
- Postdoctoral appointment at The Scripps Research Institute, La Jolla, CA -developed ***bio-derived nanoparticles***.
- Ph.D. work at Iowa State University, Ames, IA - pioneered the field of functionalized and ***multifunctionalized mesoporous silica nanospheres (MSN) including their applications in catalysis and biotech***.
- Authored over 30 technical articles, has three granted patents and several applications

Project responsibilities:

- project management
- coordinate the activities of the graduate student (to be hired)
- materials synthesis and characterization.

The Project Team

Co-PI Dr. Daniela Radu - Assistant Professor (tenure-track), Department of Chemistry at Delaware State University (since 2013).

Prior experience:

- Senior researcher at DuPont CR&D, Wilmington, DE - focus in solar research, specifically, ***nanoparticles-based solution processed thin-film photovoltaics***.
- Postdoctoral appointment at The Scripps Research Institute, La Jolla, CA – developed cyclic ***peptide nanotubes***.
- During Ph.D. work explored ***mesoporous silica applications in catalysis for biodiesel, sensing and template for polymerization of conducting nanowires***.
- authored 32 technical articles, pending patent applications and 2 granted patents.

Project Responsibilities:

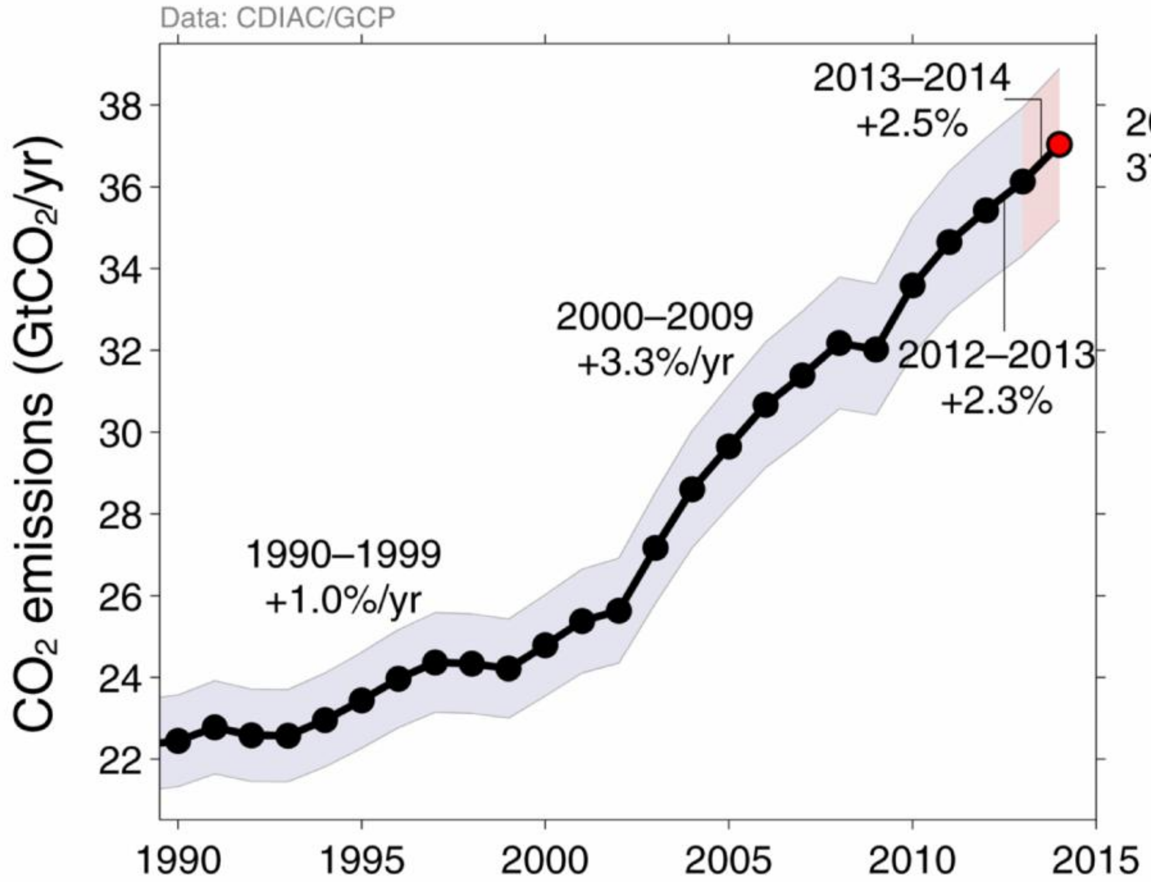
- Designing and accomplishing the CO_2 capture experiments as well as the sorbent regeneration study.
- Dr. Radu will use her experience in DOE projects reporting (*PI on DOE DISTANCE Solar award*) to assist Dr. Lai with project reporting.

Technical background and motivation for the project

- **Fossil Fuel and Cement Emissions**

Global fossil fuel and cement emissions: 36.1 ± 1.8 $GtCO_2$ in 2013, 61% over 1990

● Projection for 2014 : 37.0 ± 1.9 $GtCO_2$, 65% over 1990



Estimates for 2011, 2012, and 2013 are preliminary

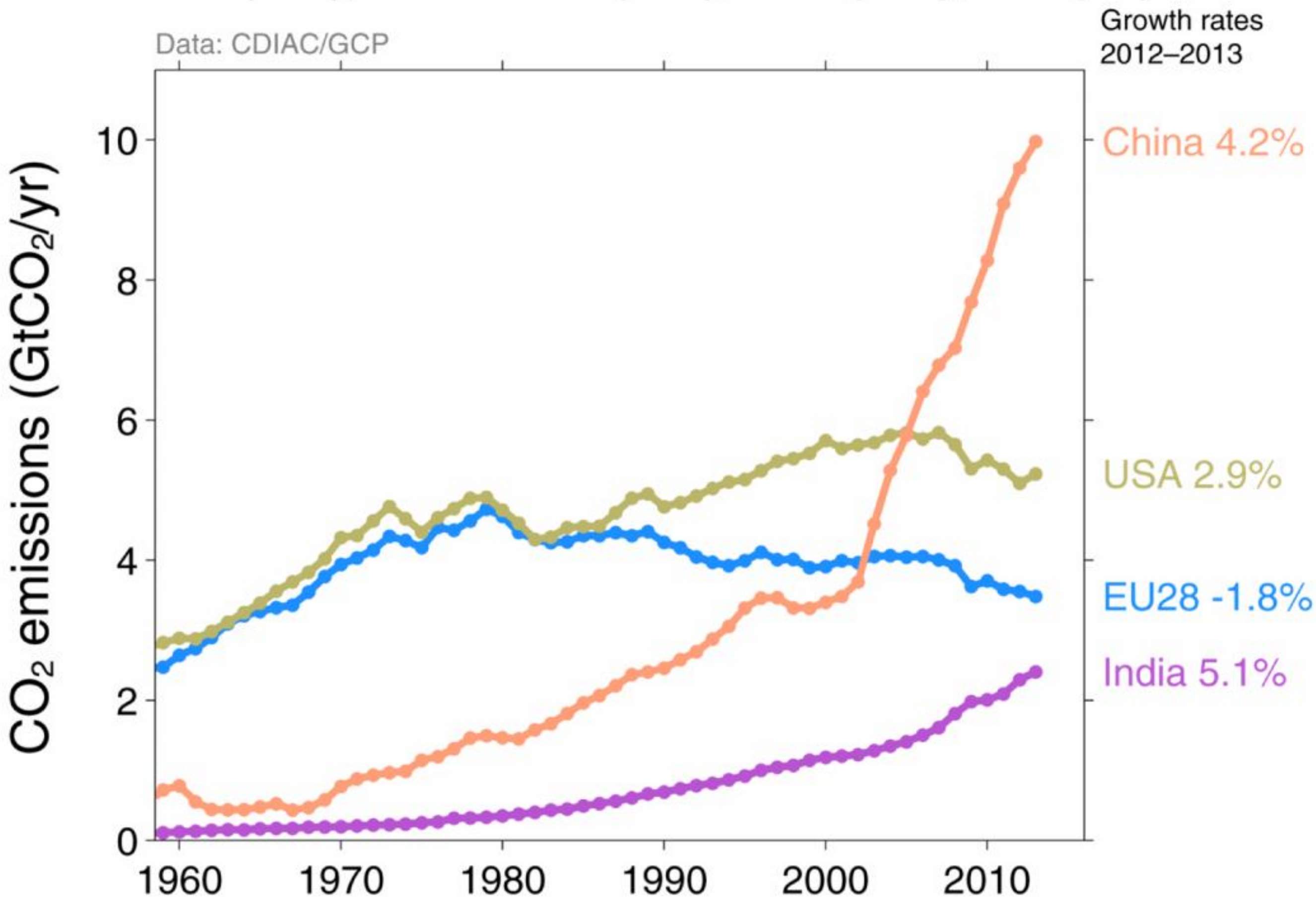
Source: CDIAC; Le Quéré et al 2014; Global Carbon Budget 2014

Technical background and motivation for the project

- Top Fossil Fuel Emitters (Absolute)

The top four emitters in 2013 covered **58%** of global emissions

China (28%), United States (14%), EU28 (10%), India (7%)



Bunkers fuel used for international transport is 3% of global emissions

Statistical differences between the global estimates and sum of national totals is 3% of global emissions

Source: CDIAC; Le Quéré et al 2014; Global Carbon Budget 2014

Technical background and motivation for the project

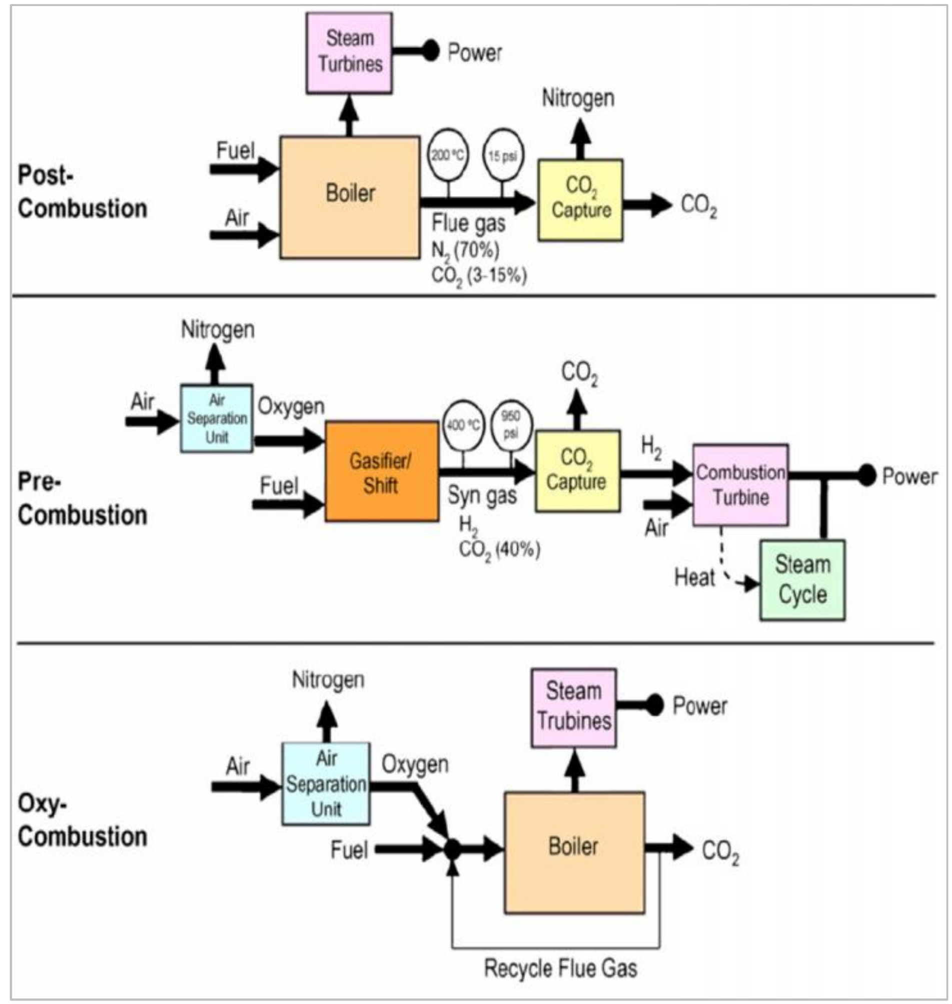
At the Climate Summit, President Obama called for further reductions in greenhouse gas emissions.

1. The implications of the 2014 carbon budget for remaining below two degrees (At the current rate of CO_2 emissions, this 1200-billion-tonne CO_2 'quota' will be used up in around 30 years – or one generation. *Nature Geoscience,* published 22 September)
2. Option to share the remaining **fossil fuel quota** to meet the two degree target (Sharing a quota on cumulative carbon emissions. *Nature Climate Change*, published 22 September)
3. How much societies will need to rely on untried **technologies** to remain below two degrees? (Betting on negative emissions. *Nature Climate Change*, published September 21th, 2014)

Technical background and motivation for the project

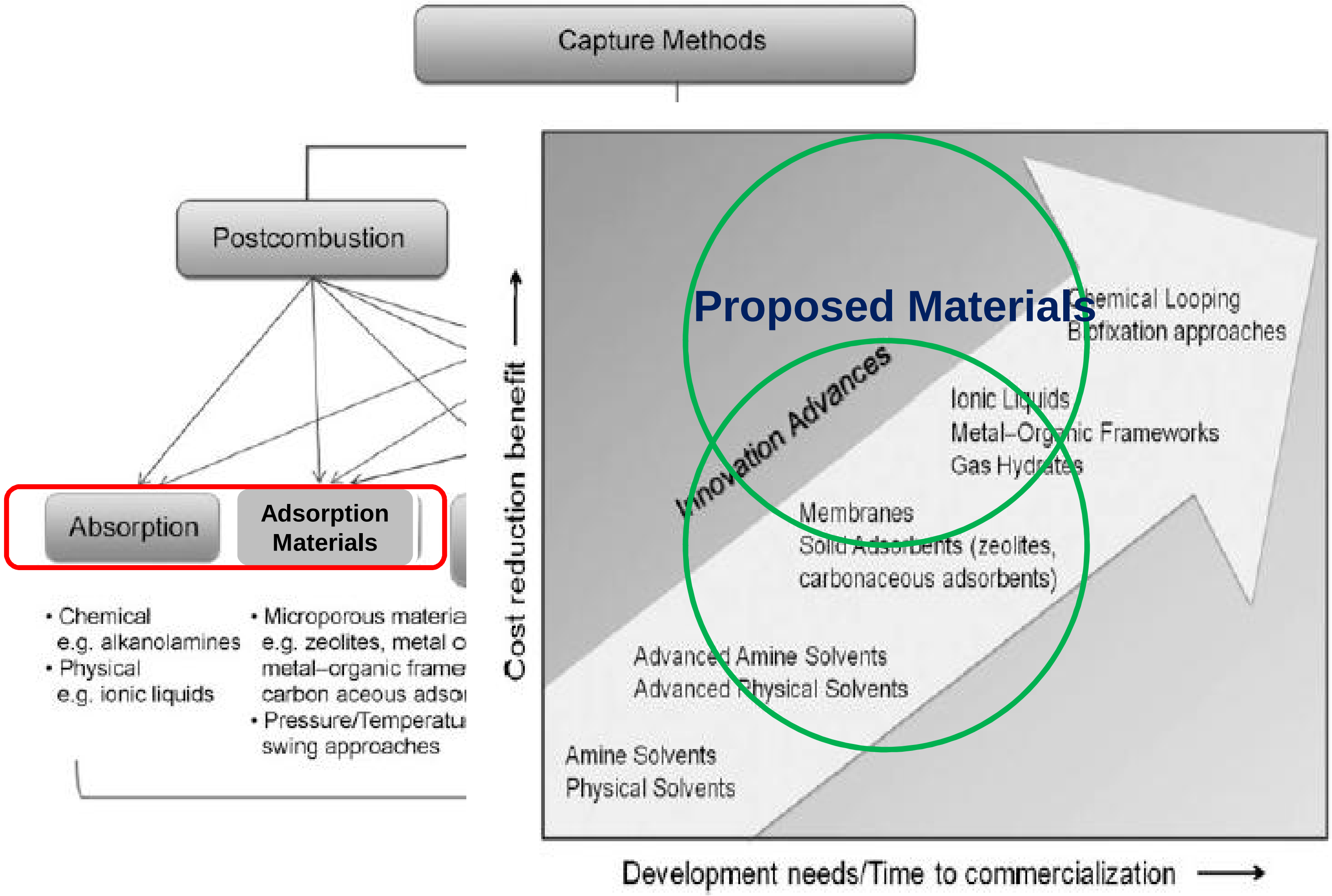
- Pathway to CO_2 Capture

  1. Post-Combustion – CO_2 is separated from other flue gas constituents either originally present in the air or produced by combustion.
  2. Pre-Combustion – carbon is removed from the fuel before combustion.
  3. Oxy-Combustion – the fuel is burned in an oxygen stream that contains little or no nitrogen.



Technical background and motivation for the project

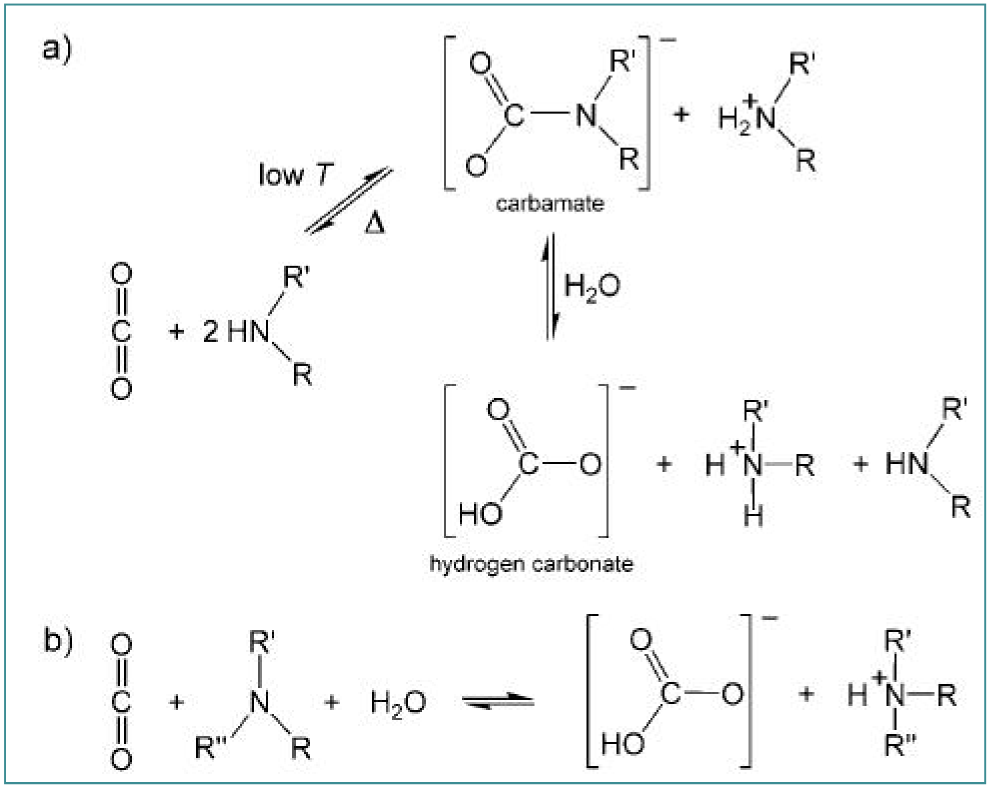
- Separation Technologies for CO_2 Capture



Materials for CO_2 capture in the context of postcombustion, precombustion, and oxyfuel processes.

Technical background and motivation for the project

- Conventional Chemical Absorption for CO_2 Capture



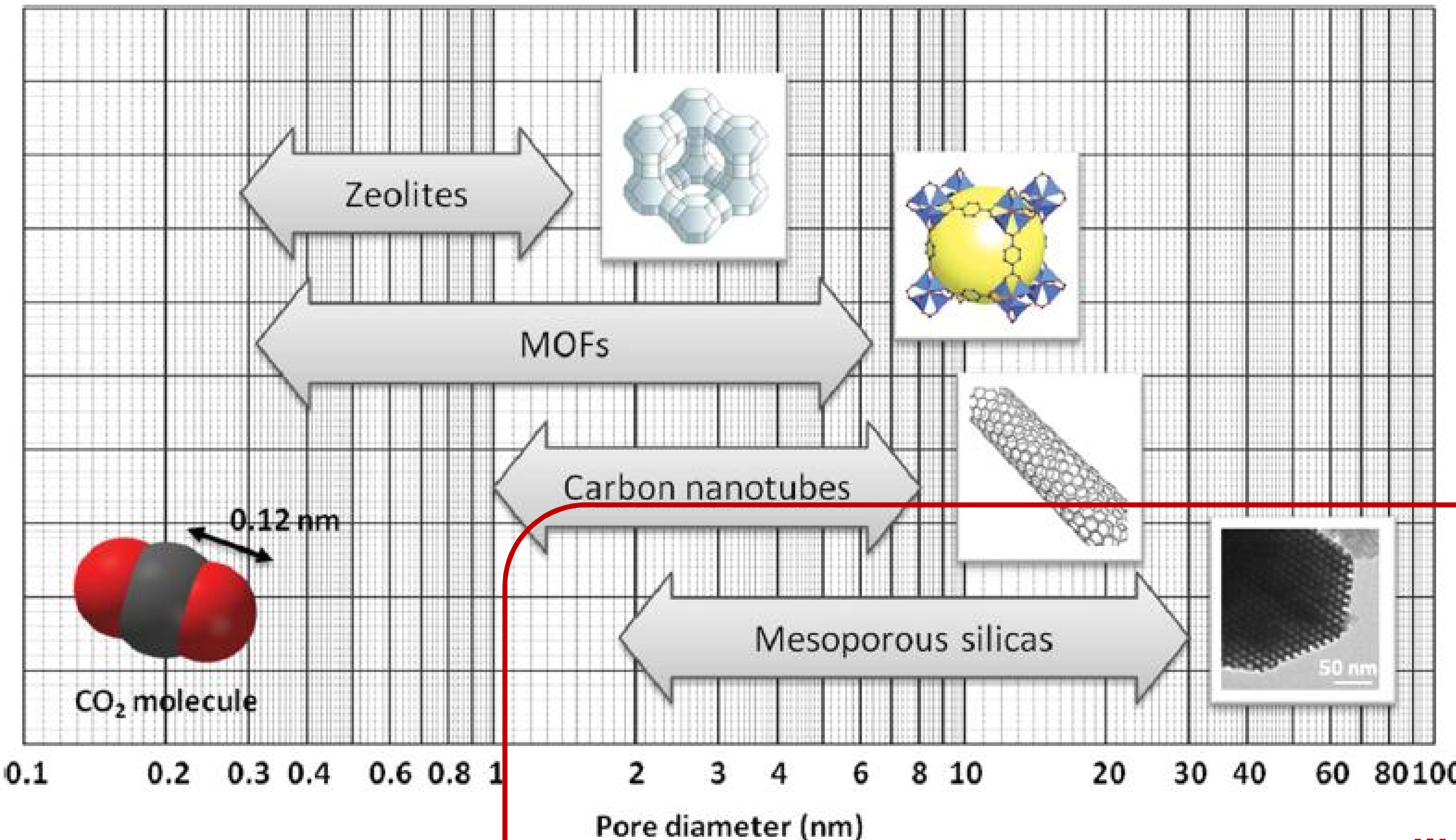
Scheme 1. General reactions for the chemical absorption of CO2 by a) primary or secondary and b) tertiary amine-containing solvents.

Complications associated with the use of *liquid amines*: **corrosion** on equipment, **oxidative degradation** of absorbents, flow problems caused by increasing viscosity relatively **high energy consumption** suggest that this method is far from ideal.

Need for Solid Sorbents

Technical background and motivation for the project

- Emerging Solid Sorbent Materials for CO_2 Capture

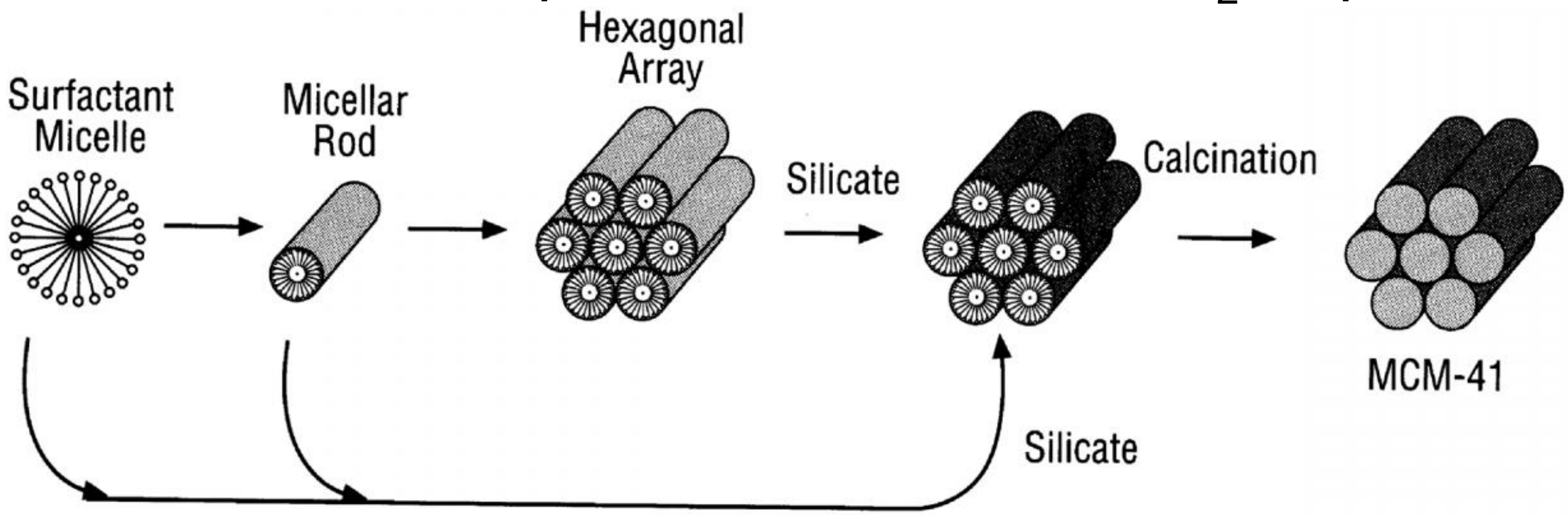


Mesoporous MCM-41 Silica

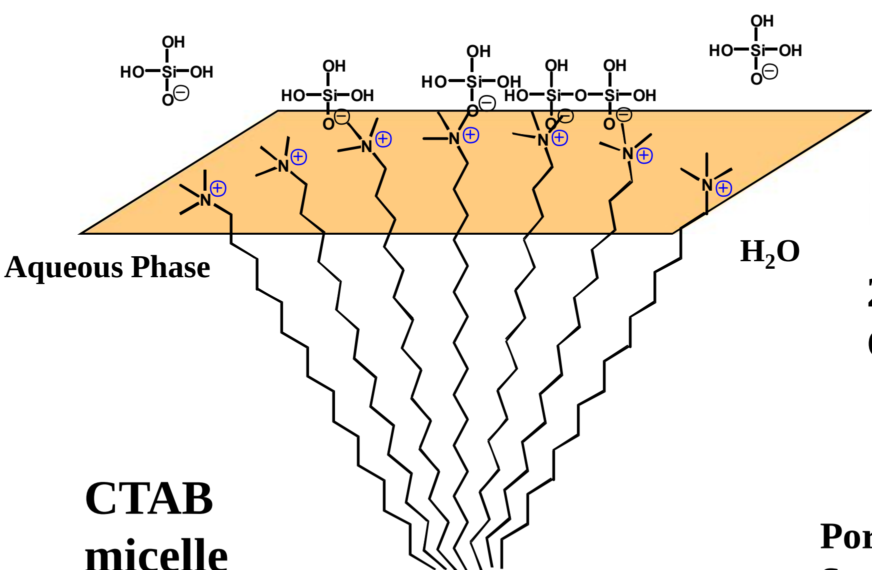
Illustrative comparison on the pore sizes of several common nanoporous materials.

Technical background and motivation for the project

- ***PHASE I.*** Nano/mesoporous Materials for CO_2 Capture

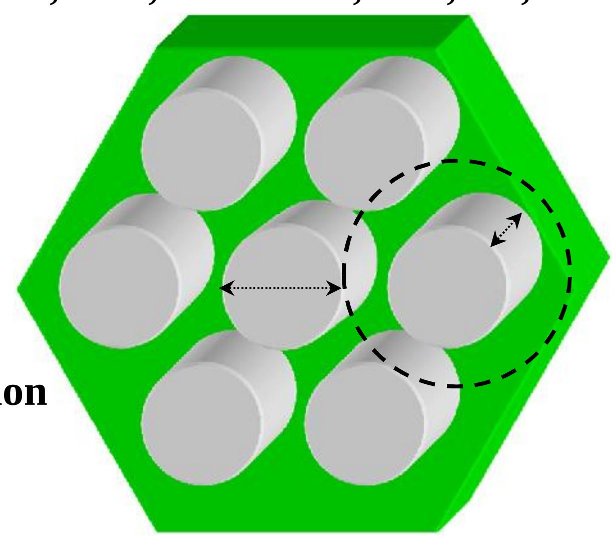


Kresge, C. T.; Leonowicz, M. E.; Roth, W. J.; Vartuli, J. C.; Beck, J. S. *Nature*, 1992, *359*, 710.



1. Sillicate

2. Calcination
Or acid extraction

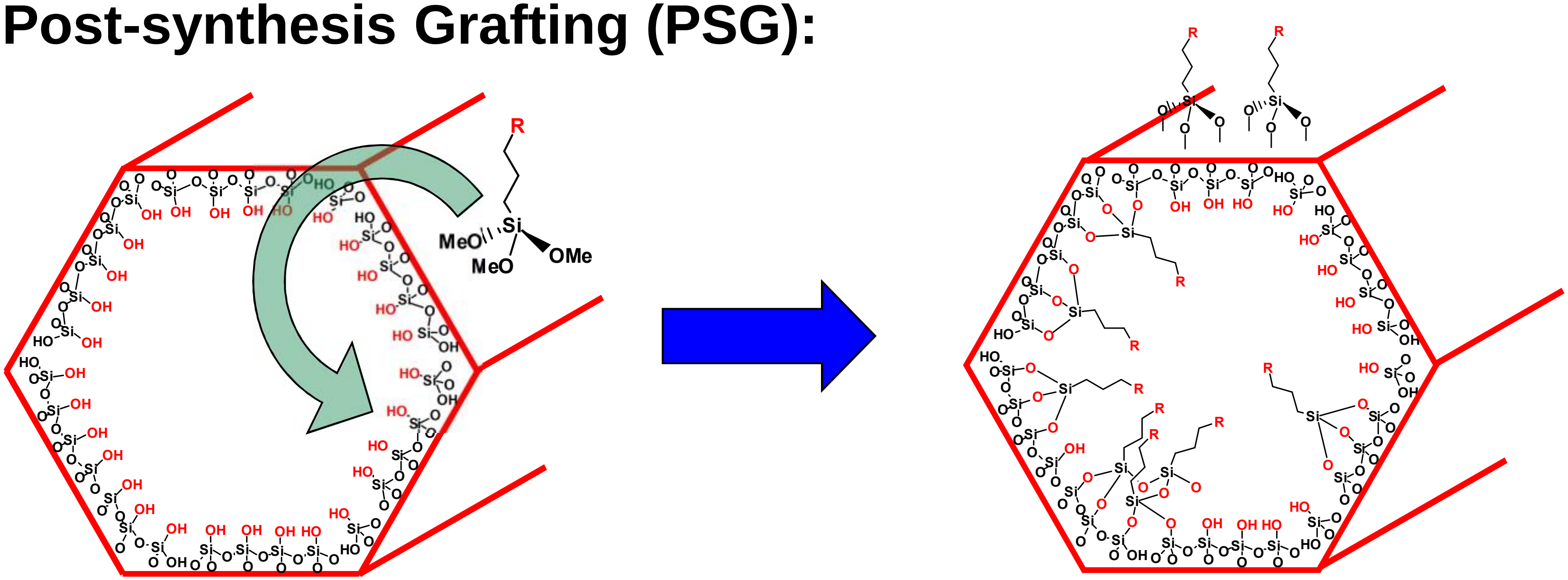


Pore Diameter = 10 to 200 Å ; Channel Depth = 0.1 to 1 Micron;
Surface Area = ~ 1000 m^2g^{-1}

Technical background and motivation for the project

- **Current Synthetic Methods for Mesoporous Silica Surface Functionalization**

- Post-synthesis Grafting (PSG):



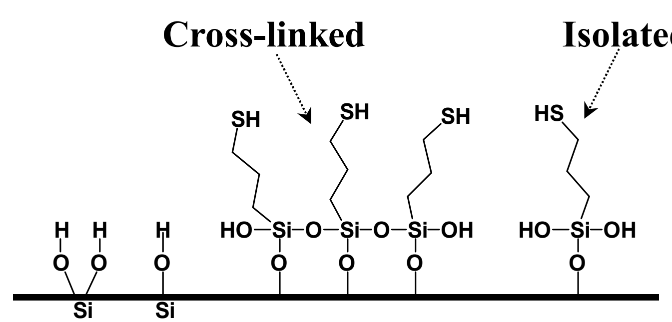
Advantages:

- **Virtually any functional group could be covalently attached to the surface**

Disadvantages:

- **Inhomogeneous surface coverage**
- **Lack of spatial control**

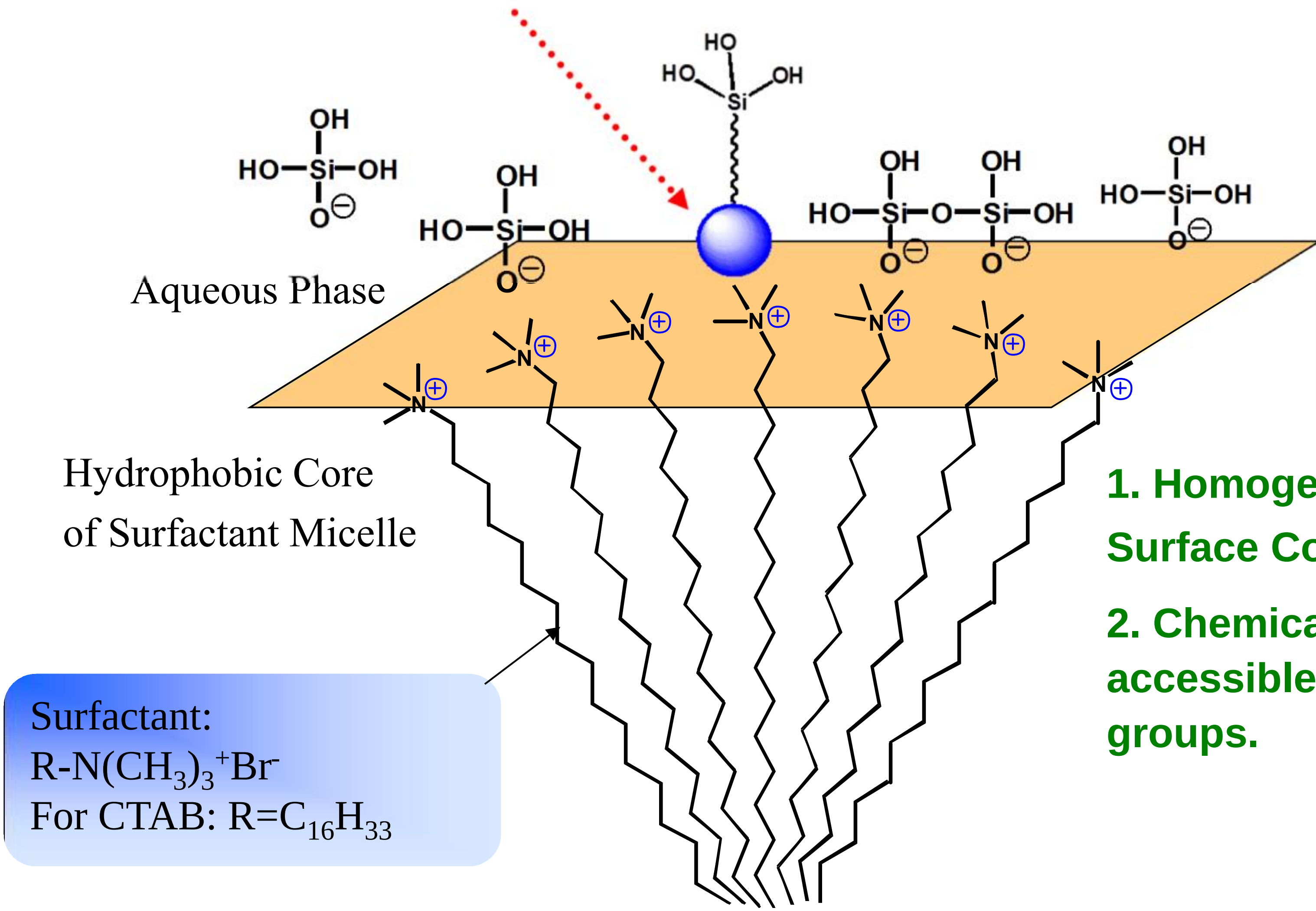
Low Surface Coverage (< 25%):



Technical background and motivation for the project

- **Introduction of functional groups *in situ*: Co-condensation**

Introduce functional groups that are *electrostatically attractive* to the ammonium surfactant head groups and able to *compete with silicate anions*.

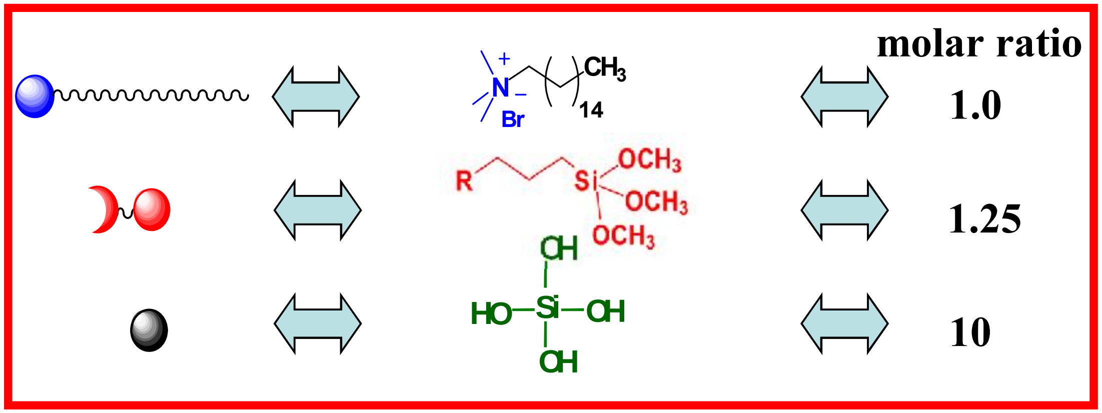


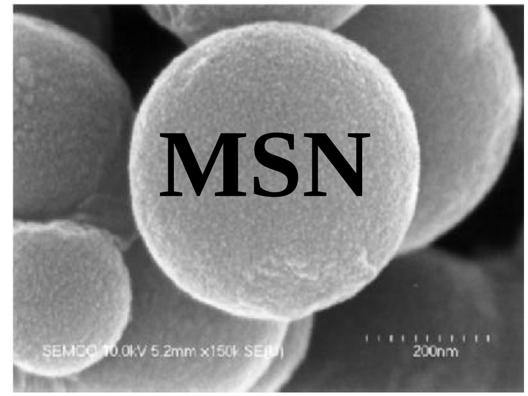
1. Homogeneous Surface Coverage

2. Chemically accessible functional groups.

Technical background and motivation for the project

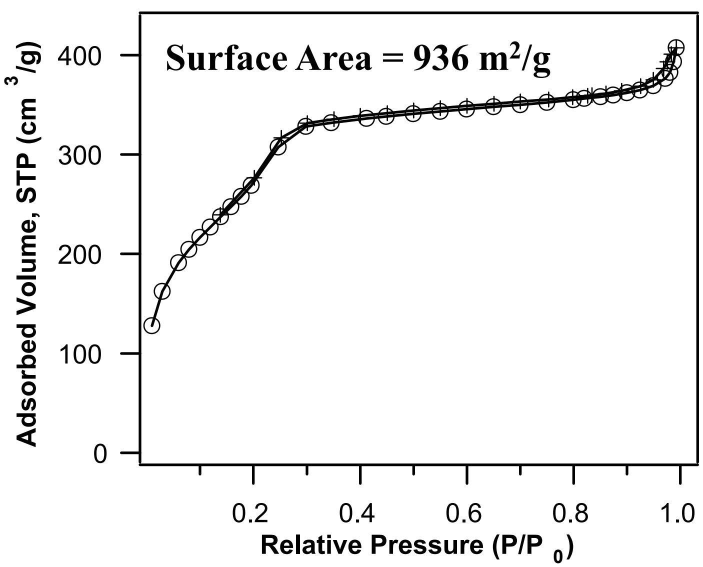
- **Functionalized Mesoporous Silica Nanospheres**



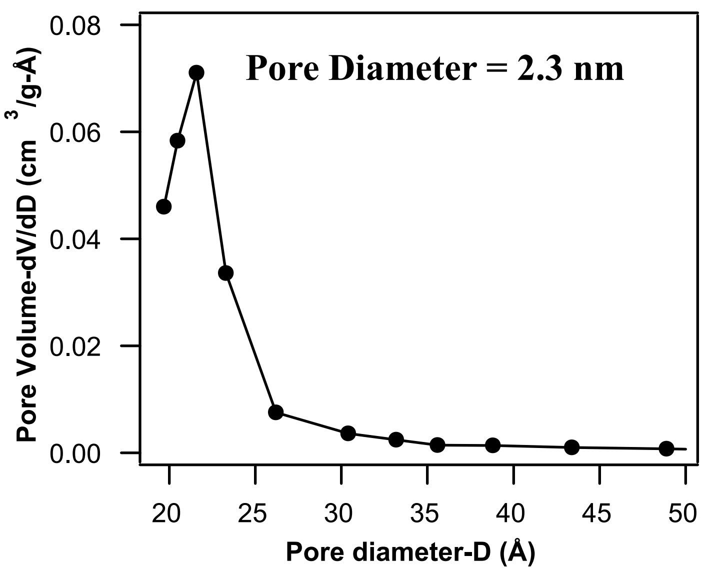


SEM of MCM-41 Nanospheres

BET N_2 Ad/desorption Isotherms:



BJH Pore Size Distribution:

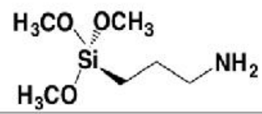
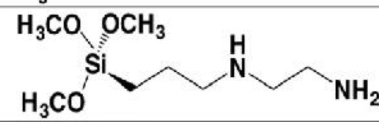
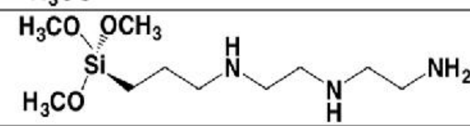


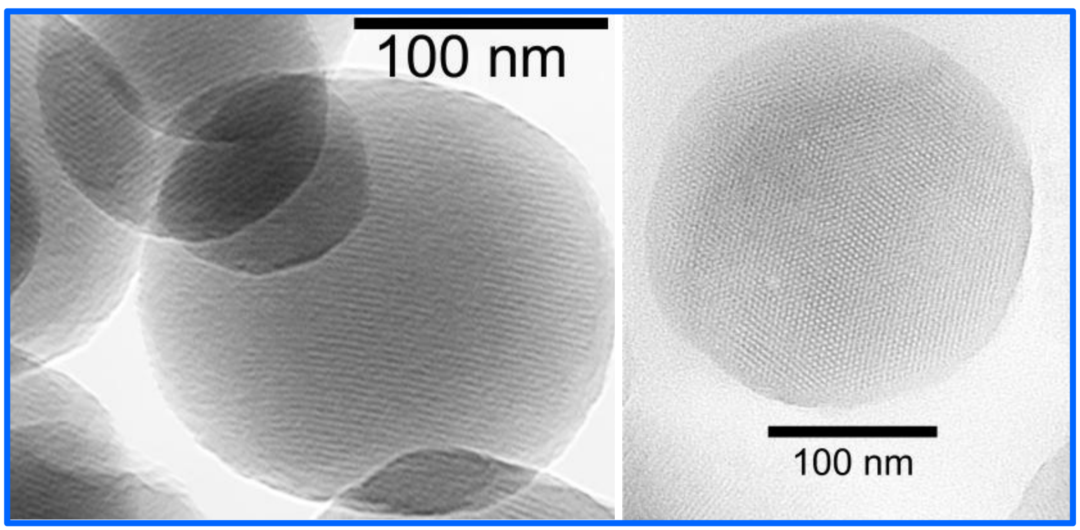
Lai, C.-Y.; Trewyn, B.G.; Jeftinija, D.M.; Jeftinija, K.; Xu, S.; Jeftinija, S.; Lin, V.S.-Y. *J. Am. Chem. Soc.*, 2003, *125*, 4451-4459.

Technical background and motivation for the project

- **Functionalized Mesoporous Silica Nanospheres**

- Multiplayer Amino Silane for Enhancing CO_2 adsorption Capacity

Name	Molecular Structure
3-Aminopropyl)trimethoxysilane	
N-(2-aminoethyl)-3-aminopropyltriethoxysilane	
N-[3-(trimethoxysilyl) propyl)] diethylenetriamine	



TEM micrographs of typical functionalized MSN

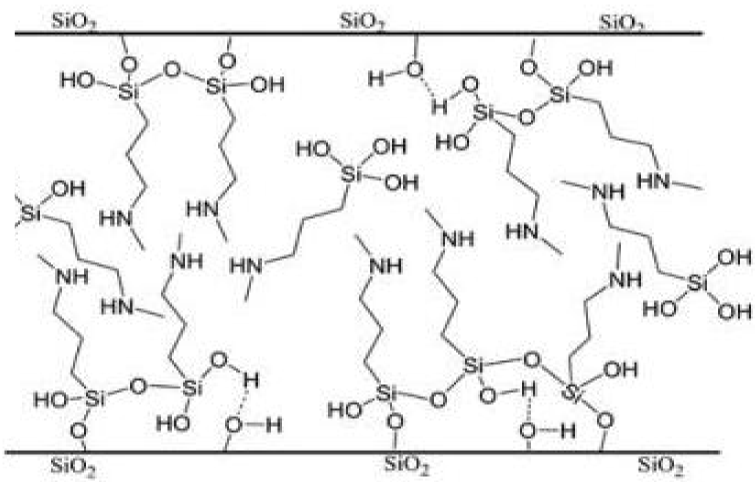
Technical background and motivation for the project

- **Pitfalls in Designing MSN for CO_2 capture:**

  -Pore Blocking Hindering Amine Permeability

  <u>Typical MSN</u>: cylindrical pores of drive close-packing of amine groups and render inner amino groups inaccessible for CO_2 capture

Retard Adsorption Kinetics for CO_2 DIFFUSION



Scheme 2. 3-(Methylamino)-propyltrimethoxysilane (MAP) functionalizated MSN pore

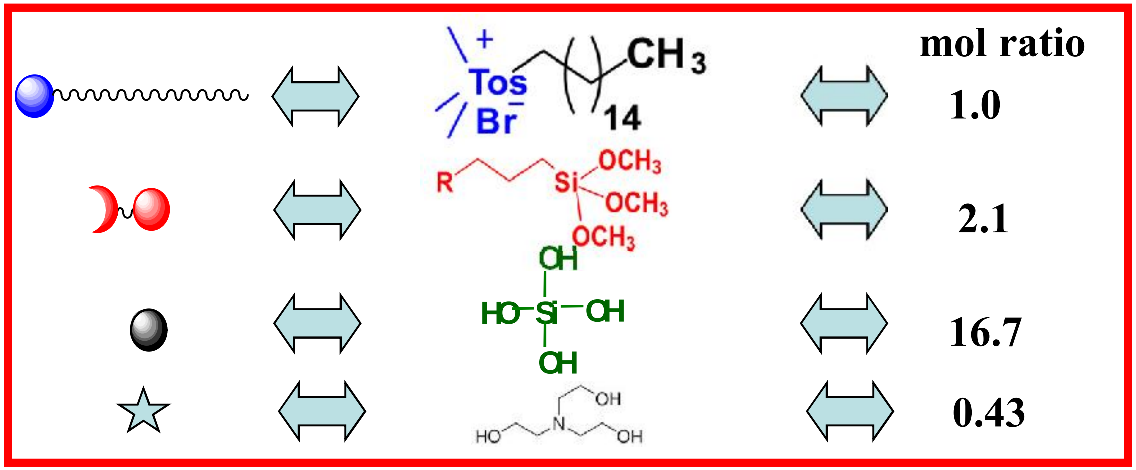
SOLUTION:

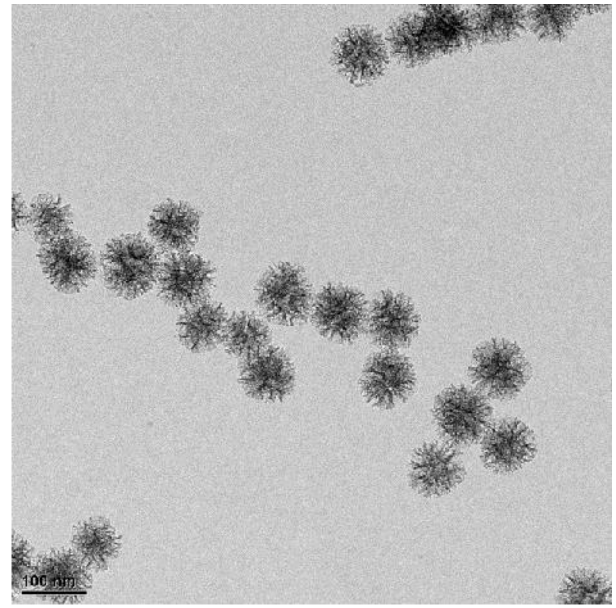
Large Pores–MSN

(Hierarchical-pores MSN)

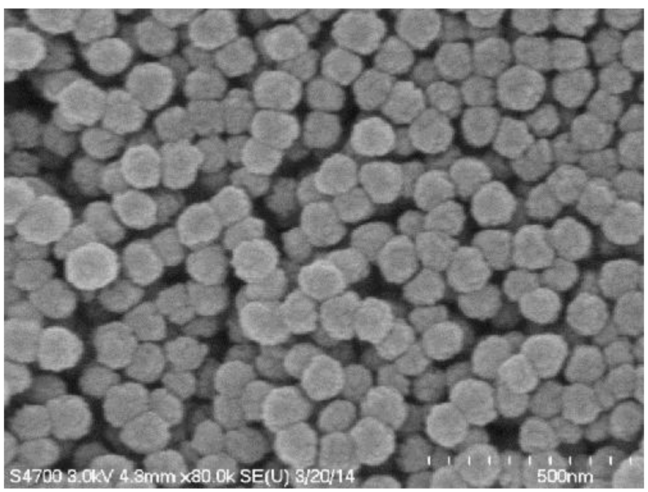
Technical background and motivation for the project

- **Strategy for Synthesizing Hierarchical-Pores NanoSilica**
  - **Surfactant template changes**
  - **Directing agents**





TEM of NSN Nanospheres



SEM of NSN Nanospheres

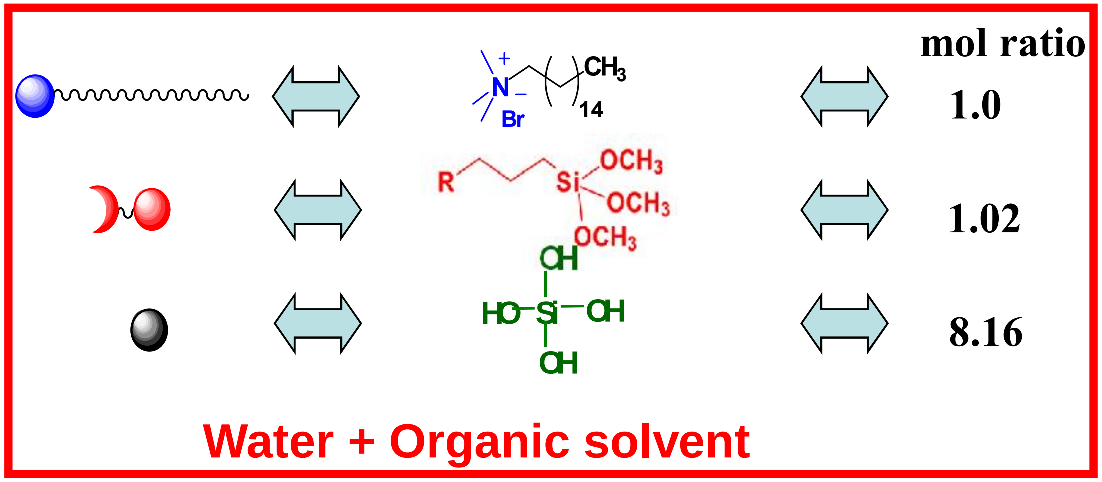
Pore Volume = 1.22 cm^3/g

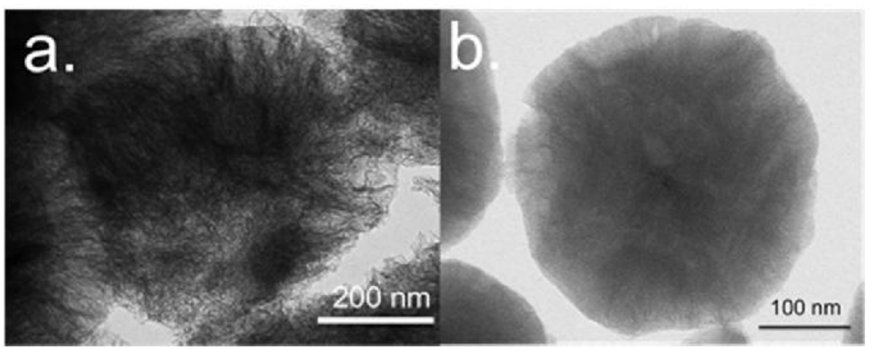
BJH Pore Diameter = 8.43 nm

BET Surface Area = 607.82 m^2/g

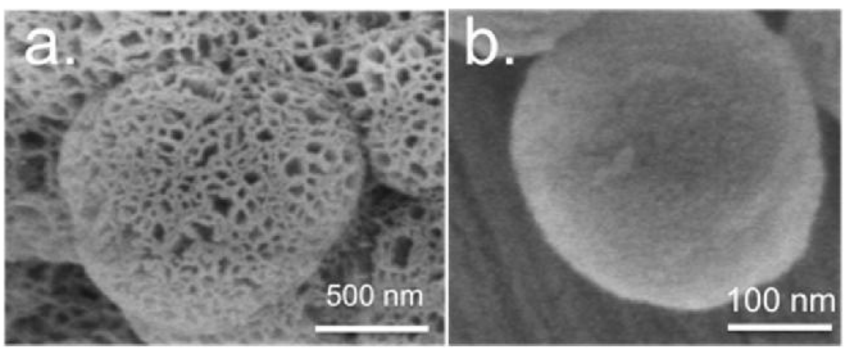
Technical background and motivation for the project

- **Strategy for Synthesizing Hierarchical-Pores NanoSilica**
  - **Co-solvents**





TEM images of NSN-1 (a) and NSN-3(b) showing the nanosheet-structure of the two novel materials



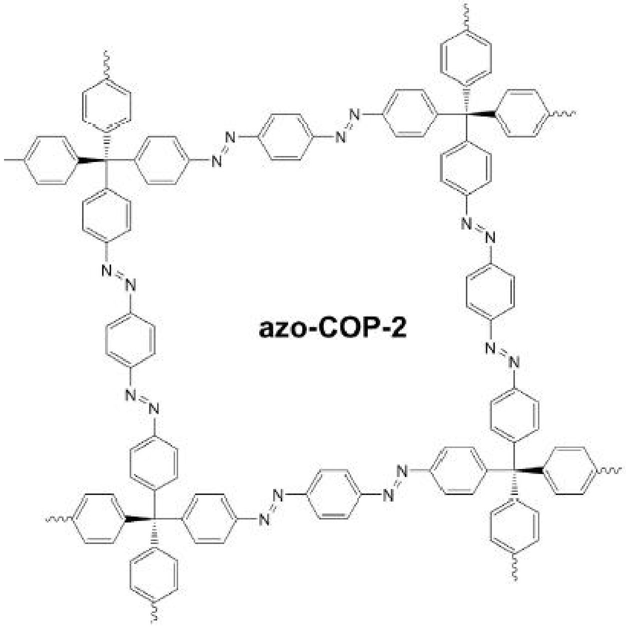
SEM images of materials NSN-1 and NSN-3

Technical background and motivation for the project

PHASE II. Increasing CO_2 capture by introducing "Nitrogen-repellent" components

Prior approach[1]: **azo-bridged, nitrogen-rich, aromatic, water stable, nanoporous covalent organic polymer (Azo-COP) *N_2-phobic*** nanoporous covalent organic polymers.

Disadvantage: Cumbersome organic synthesis.

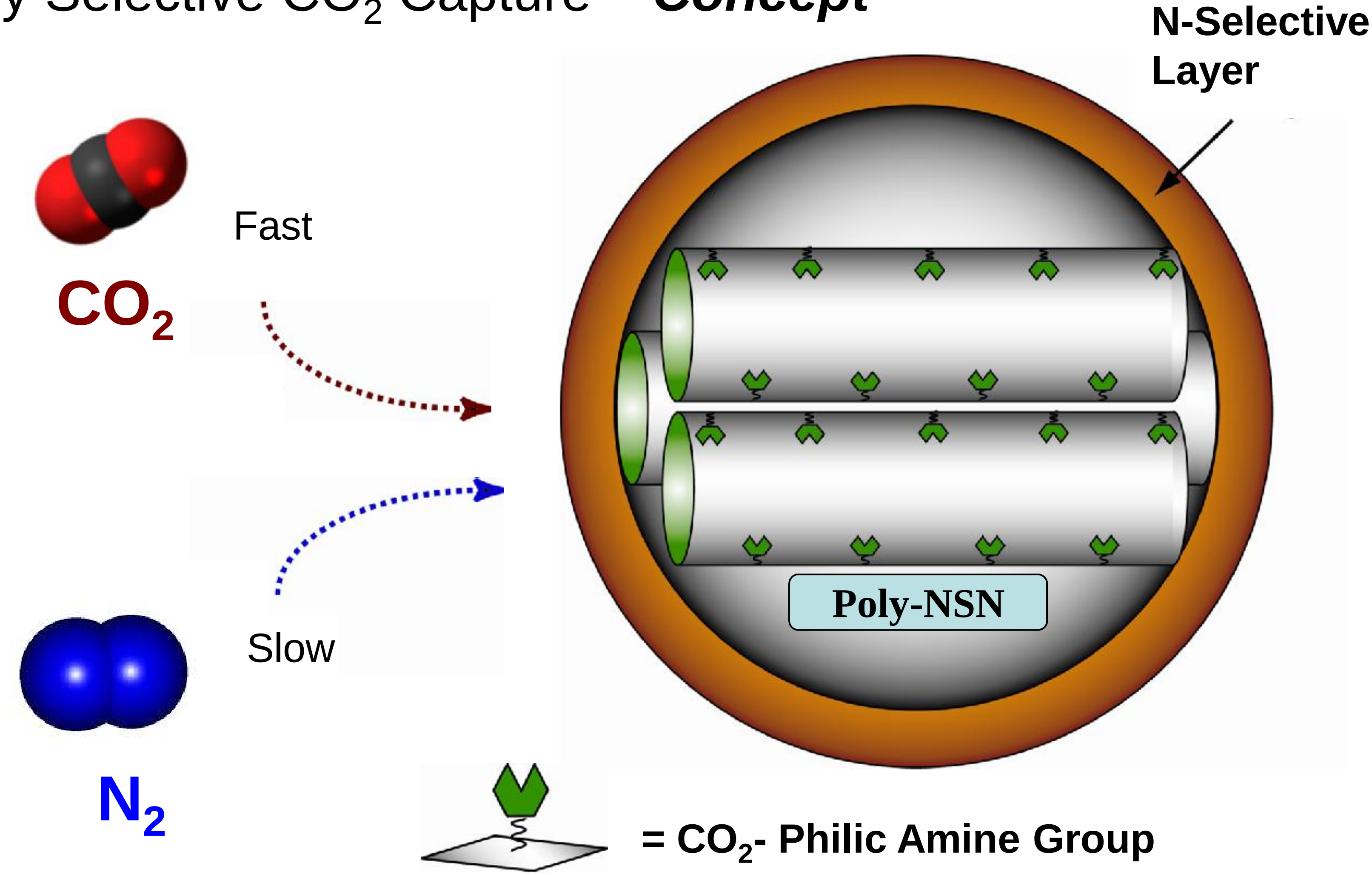


Our approach: Bi-Functional Nanosheet-made Silica Nanosphere Adsorbent for N_2-Phobic Highly Selective CO_2 Capture

1. Patel, H. A.; Hyun Je, S.; Park, J.; Chen, D. P.; Jung, Y.; Yavuz, C. T.; Coskun, A., Unprecedented high-temperature CO_2 selectivity in N_2-phobic nanoporous covalent organic polymers. *Nat Commun* **2013,** *4*, 1357.

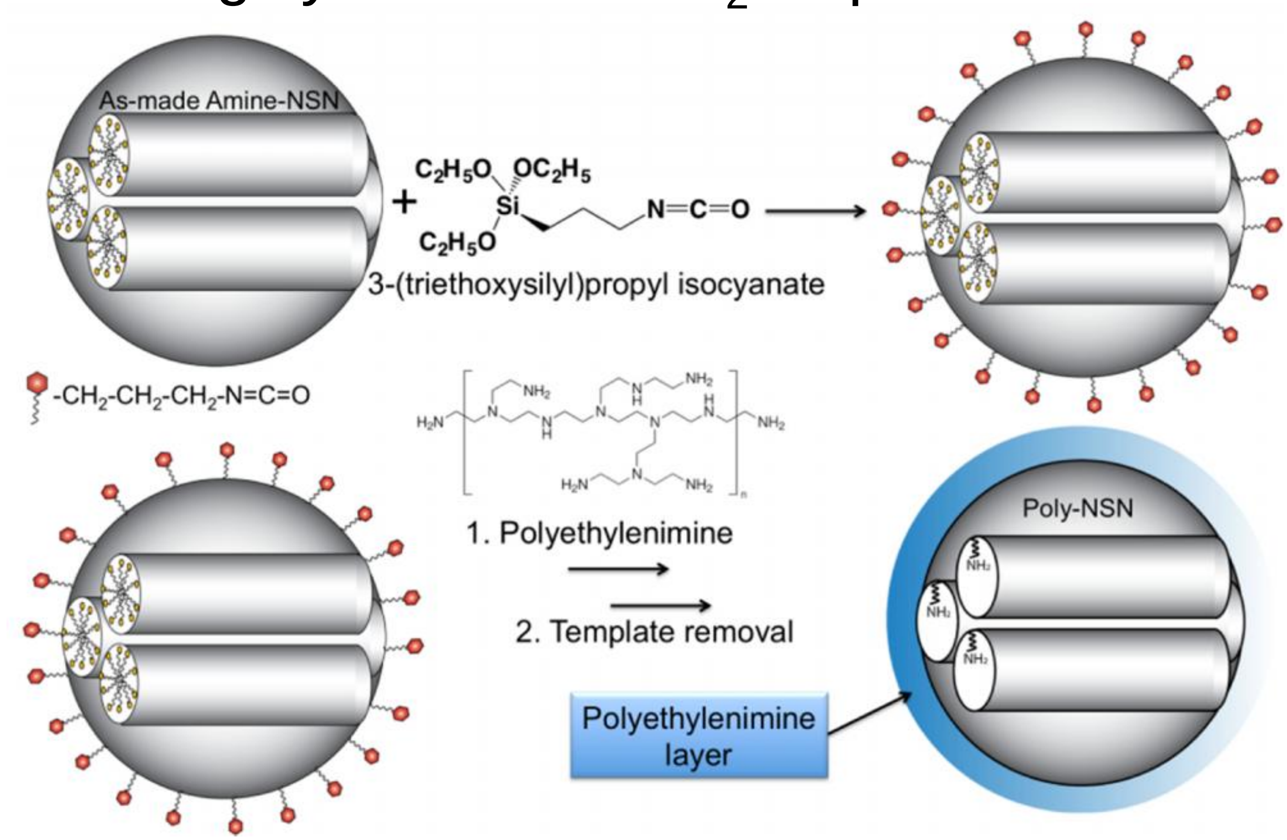
Technical background and motivation for the project

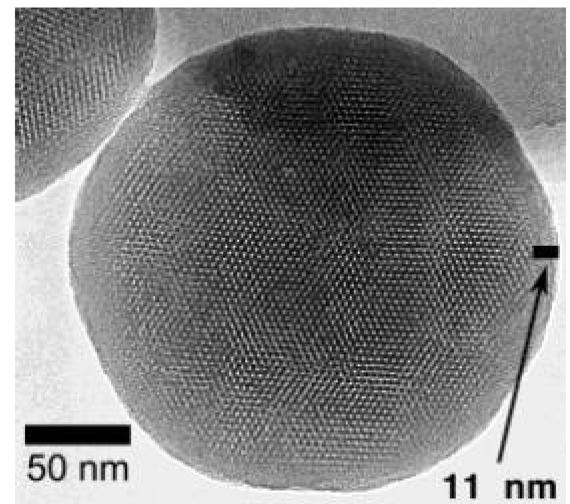
- Diffusion Controlled Mesoporous Silica Nanosphere Adsorbent for Highly Selective CO_2 Capture – ***Concept***



Technical background and motivation for the project

- Diffusion Controlled Mesoporous Silica Nanosphere Adsorbent for Highly Selective CO_2 Capture



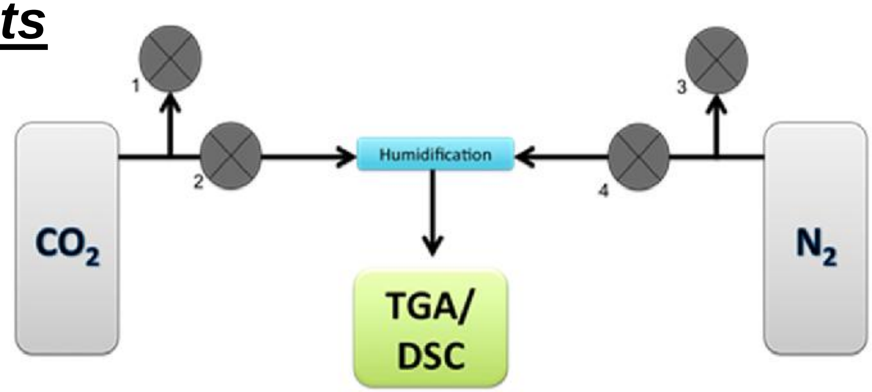


Differential functionalization methodology applied to NSN for further functionalization with polymeric "gate-keeper" groups.

Technical background and motivation for the project

- NSN-based adsorbent for highly-efficient CO_2 capture

  - ***<u>Carbon dioxide cycling experiments</u>*** will be performed on TGA Instruments analyzer using:
  a). 15% CO_2 in N_2;
  b). CO_2 ;
  c). N_2 at a predetermined flow rate for all gases.

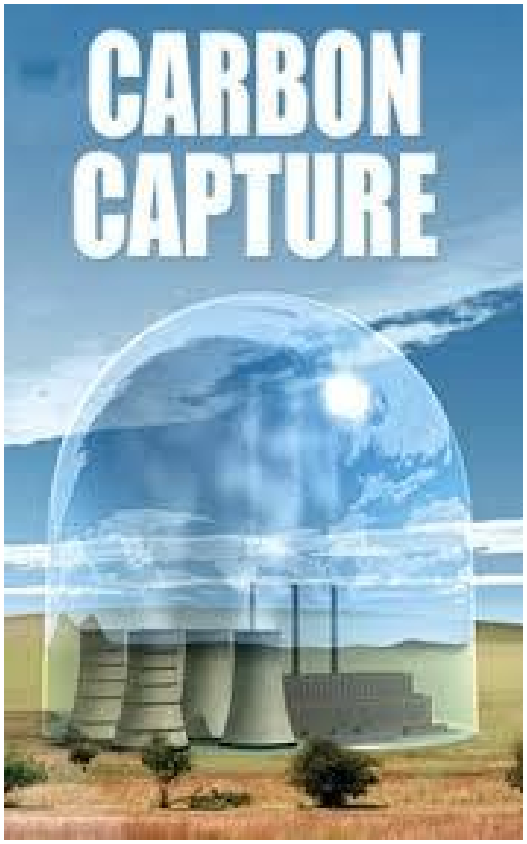


Scheme 3. TGA setting for CO_2 capture experiments

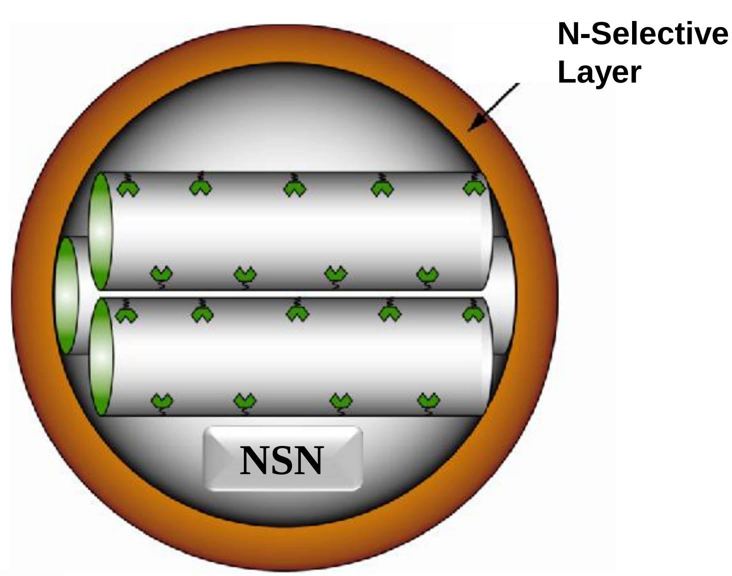
- Separation From Gas Mixture

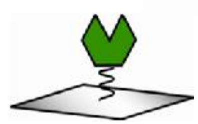
➡ CO_2 Adsorption and N_2 Separation on Flue Gas Mixture

Potential significance of the results of the work



- The most significant challenge for CO_2 capture at present, the large energy penalty associated with the capture process.
- Current technologies, approximately 70% of the cost of CCS is associated with the selective capture of CO_2 from the power plant flue gas.
- Our approach involve dramatic costs cut by applying the capture platform in form of **PAINT**





= CO_2- Philic Amine-based Functionality

Potential significance of the results of the work

Outcomes

a) A graduate student fully trained in materials synthesis and characterization.

b). A new technology for fabrication of nanosheet-made mesoporous silica (NSN) platform with high CO_2 capture capacity at low-cost and with high regeneration capacity.

c). A new technology forfabrication of a polymer coated nanosheet-made mesoporous silica platform with nitrogen-phobic properties and high CO_2 capture capacity at low cost and with high regeneration capacity.

Potential significance of the results of the work

Impacts

a). *Social—People.* Training of a graduate student from an underrepresented group will contribute to increasing diversity of the workforce.

b). *Technical—Efficient* CO_2*-capture-technologies*: the materials developed will remove CO_2 from air in existing fossil-burning plants.

c). *Other technical benefits*. Applicability to other sectors.
Ex. alkaline fuel cells (AFCs) and iron-air batteries require ***CO_2–free O_2 sources*** to avoid electrolyte side reactions → inexpensive CO_2 adsorbents could solve issues associated with the operation of AFCs (provided current air purification methods lack of feasibility and high costs).

Relevancy to Fossil Energy

- Existing post-combustion CO_2 control systems separate CO_2 from the flue gas produced by conventional coal combustion in air. The flue gas is at atmospheric pressure and has a CO_2 concentration of 10-15 % (by volume).

- Capturing CO_2 under these conditions is challenging because:

  - The low pressure and dilute concentration dictate a high total volume of gas to be treated.
  - Trace impurities in the flue gas tend to reduce the effectiveness of the CO_2 separation processes.
  - Compressing captured CO_2 from atmospheric pressure to pipeline pressure (1,200-2,200 pounds per square inch) represents a large parasitic energy load.

- The project aims to develop a novel, low cost, scalable platform that is anticipated to work at low CO_2 partial pressure and that the system will not be impaired by impurities due to hierarchical structure of the platform.
- In addition, we developed a strategy to increase CO_2 Capture efficiency. The design will render the platform nitrogen-phobic by engineering the polymeric layer to act as a gate-keeper to exclude nitrogen → increase capacity for CO_2.

Statement of Project Objectives (SOPO)

Objective 1. Demonstrate a nanosheets-made silica nanosphere (NSN) platform as solid sorbent with spatial control of CO_2 capture amine functionality and high amine loading at least 7 mmol N/g sorbent, with hybrid absorption–adsorption capacity of at least 5 mmol CO_2 per gram of NSN sorbent.

Objective 2. Perform parametric and long-duration tests to demonstrate that the technology meets performance target of achieving of CO_2 capture at >90% of simulated flue gas with 15% CO_2.

Objective 3. Engineer a gate-keeping polymeric layer of NSN surface (PolyNSN), designed to increase selectivity of CO_2 capture by excluding N_2 from in the capture process.

Objective 4. Perform parametric and long-duration tests to demonstrate proof-of-concept of nitrogen exclusion in selective CO_2 capture in PolyNSN.

Project milestones, Budget, and Schedules as related to SOPO tasks

SOPO ID Number | Item Description | Performer | Start Date | End Date

SOPO ID Number	Item Description	Performer	Start Date	End Date
TASK 5.0	PolyNSN selective CO_2 capture experiments	RADU	**03/01/16**	**08/31/17**
TASK 6.0	Conduct long-term tests to determine the chemical and physical stability of the sorbents.	RADU	06/01/15	08/31/17
Final Deliverables	***<u>Final Deliverable 1:</u>*** Demonstrate a high performance NSN platform with at least 5 mmol CO2/g sorbent and high robustness and regeneration capacity (100%). ***<u>Final Deliverable 2:</u>*** Demonstrate a high performance PolyNSN platform with at least 5 mmol CO2/g sorbent, high robustness and regeneration capacity (100%) capability to exclude N2 .	LAI & RADU		**08/31/17**

and regeneration capacity (100%)
capability to exclude N2 .

Project Risks and Risk Management Plan

- The risks associated with this project are related to budget (costs) and to health and safety.

Project Costs: Excess spending on the budget.
The risk response is based on two strategies:
• Avoid/Mitigate by Preventing: Strict documentation will be kept to avoid overspending.
• Mitigate by Recovering: assess problem extent and report to DOE. If costs are in year 1 or 2, allowance will be request for recovering from Budget Year 3.

Health and Safety: Goal is ZERO on safety incidents and health hazards.
The risk response is based on two strategies:
• Avoid/Mitigate by Preventing: SOPs will be associated with all instruments used in the project and all substances used will have MSDS sheets in electronic (lab computer)and hardcopy format in the laboratory.
• Accept: Safety incidents will be treated per University policy and will be further reported to DOE.

Other Relevant *Aspects of The Project Management Plan (PMP)*-Budget

Category	Budget Year1	Budget Year2	Budget Year3	Total Costs
a. Personnel	$32,944	$32,944	$32,944	$98,832
b. Fringe Benefits	$3,972	$3,972	$3,972	$11,916
c. Travel	$4,000	$4,000	$4,000	$12,000
d. Equipment	$24,673	$0	$0	$24,673
e. Supplies	$7,500	$7,500	$7,500	$22,500
f. Contractual	$0	$0	$0	$0
g. Construction	$0	$0	$0	$0
h. Other	$3,000	$3,000	$2,600	$8,600
i. Total Direct Charges (sum of 6a-6h)	$76,089	$51,416	$51,016	$178,521
j. Indirect Charges	$23,651	$23,651	$23,467	$70,769
k. Totals (sum of 6i-6j)	$99,740	$75,067	$74,483	$249,290

Other Relevant Aspects of The Project Management Plan (PMP)-*Decision Points*

- **Success Criteria at Decision Points**

TASK 1.0 – Project Management and Planning (please see the Project Management Plan).

TASK 2.0 (Budget period 1) *Preparation and characterization of NSN-solid sorbents*

Success: obtaining the material with spherical morphology and particle size <1 micron, and surface area >1400 m2/g and amine loading at 7 mmol/g.

***Go/No-GO Decision Point*: Low surface area and low amine loading below performance targets.**

TASK 3.0 Determine the CO_2 absorption and regenerative capacity of NSN materials.

Success: Demonstrate an NSN platform with a capacity of at least 4 mmol CO_2/g sorbent capable to remove >90% of the CO_2 from a simulated flue-gas mixture containing 15 vol% CO_2 at 40-70 °C. Demonstrate an amine NSN sorbent with 100% absorption capacity regeneration.

Other Relevant Aspects of The Project Management Plan (PMP)-*Decision Points*

<u>TASK 4.0 Gate-keeping layer fabrication on NSN surface</u>

Success: Demonstrate presence of a polymeric layer on the surface of the NSN via TEM.

Go/No-GO Decision Point: Presence of a polymeric layer is not identified.

<u>TASK 5.0 PolyNSN selective CO_2 capture experiments</u>

Success: Demonstrate a PolyNSN platform with an improved capacity of at least 5 mmol CO_2/g sorbent capable to remove >90% of the CO_2 from a simulated flue-gas mixture containing 15 vol% CO_2 at 40-70 °C. Demonstrate a PolyNSN sorbent with 100% absorption capacity regeneration.

Go/No-GO Decision Point: No improvements in absorption capacity are observed for PolyNSN in comparison with NSN.

<u>TASK 6.0</u> Conduct long-term tests to determine the chemical and physical stability of the sorbents.

Success: Demonstrate a sorbent with high chemical and mechanical stability that retains 95% of absorption capacity within 6 months, and at least 50% over two years.

Project Status

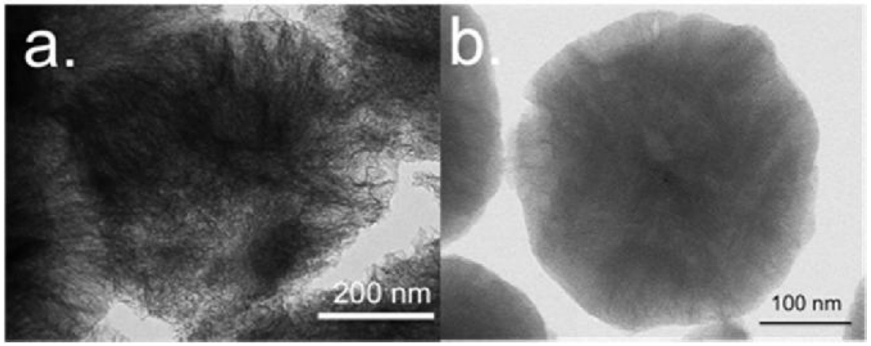
SOPO ID Number	Item Description	Performer	Start Date	End Date
Task 2.0	Preparation and characterization of NSN-solid sorbents	LAI	**09/01/14**	**05/31/15**
Subtask 2.1	Silica Sorbents Preparation – Synthesis of NSN	LAI	09/01/14	05/31/15
Subtask 2.2	*Silica Sorbents Characterization*	LAI	09/01/14	05/31/15

Task 2.0 **Preparation and Characterization of NSN-solid sorbents**

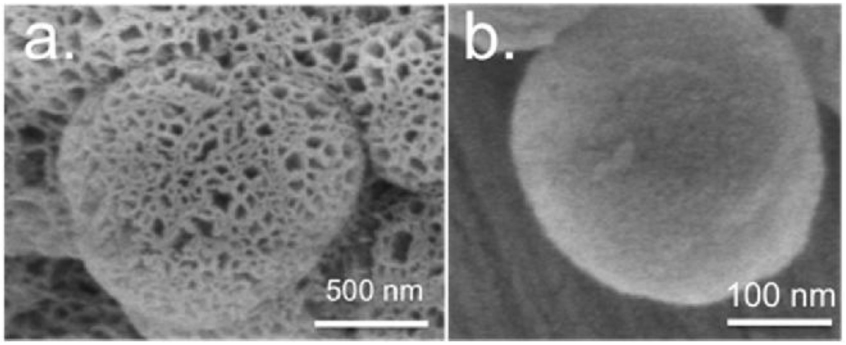
STATUS: ***Ongoing;***

- **Few materials fabricated and ready for characterization**
- Images below took at University of Delaware
- New TEM/SEM microscope on site (installed – DOD Award,

PI Daniela Radu)



TEM images of NSN-1 (a) and NSN-3(b) showing the nanosheet-structure of the two novel materials



SEM images of materials NSN-1 and NSN-3

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- **Department of Chemistry,** Delaware State University

Thank you for your attention!

Questions?