Functional Nanoparticle-Augmented Surfactant Fluid for Enhanced Oil Recovery in Williston Basin

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Current Problem and Need

- **Bakken Petroleum System**

The Bakken Formation in Williston basin is one of the largest contiguous deposits of oil and natural gas in the United States

DMR’ s assessment (2008) of the oil potential of the Bakken Formation in North Dakota: up to 167 billion barrels of oil (oil in place) .

Low recovery: 5-10% of OOIP

- **Imperative Need to Increase Oil Recovery in Bakken**

Each 1% of additional recovery amounts to nearly 1.7 billion barrels of additional produced oil and associated natural gas.

Current EOR Techniques and Challenges

▪ CO_2 EOR

- Availability of CO_2 in quantities and prices
- Not suitable for Low pressure reservoir/heavy oil

▪ Surfactant Imbibition in Bakken

- The low mobility of surfactant results in low EOR response and notable amount of surfactants remained inside rocks. Loss of surfactants.
- The waste of surfactants increases the cost of oil production and potential environmental impact.

Objective of This Proposal

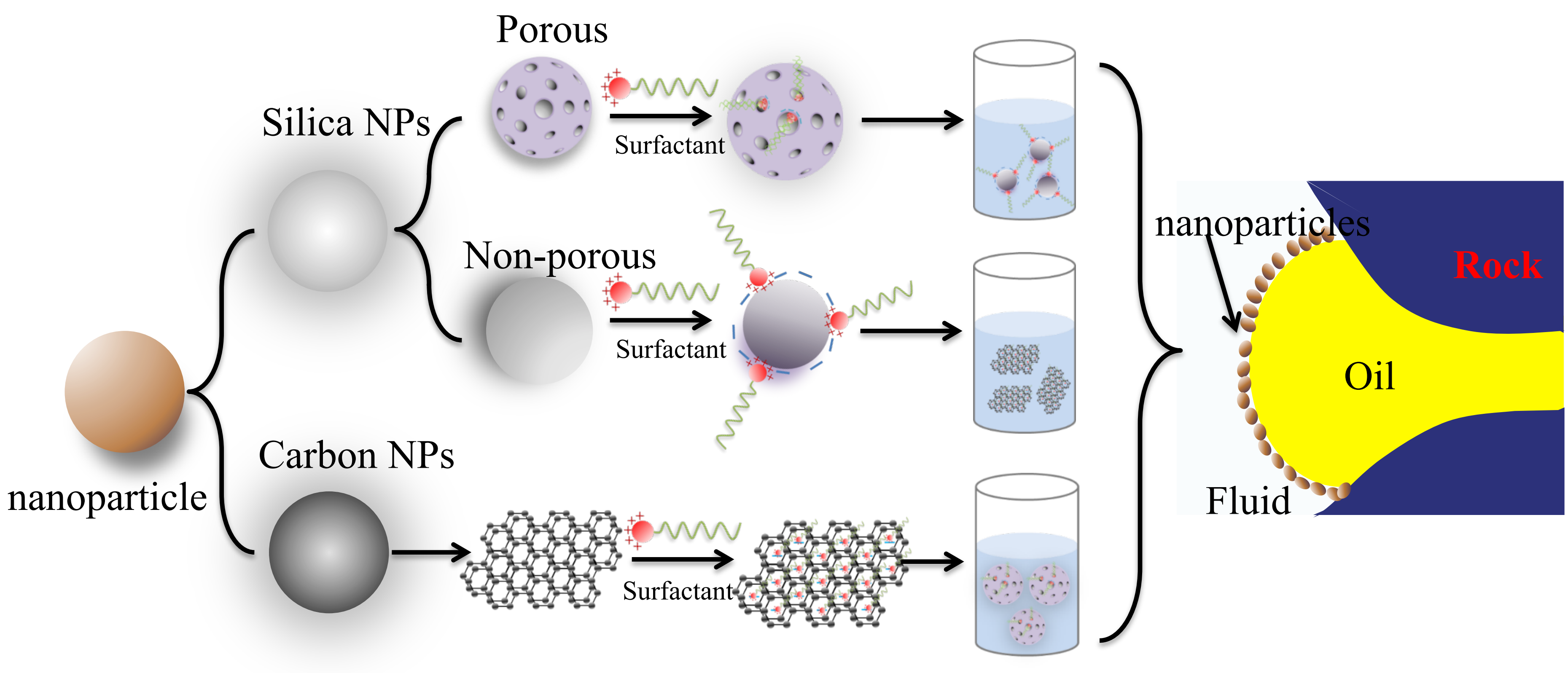
To address a question:

How can we develop a good EOR fluid to successfully

1. **Penetrate rocks,**
2. **Displace oil locked in micro/nano-pores of tight rocks,**
3. **Carry the oil out of the rocks.**

Our Design

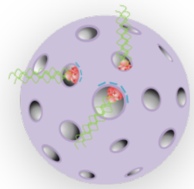
Development of Nanoparticle Enriched Surfactant for EOR

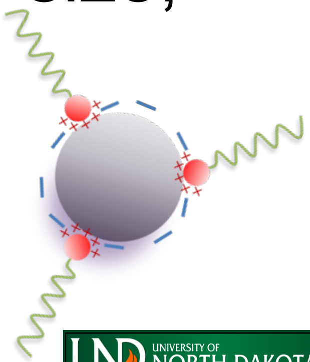


Altering the rock wettability, reduce interfacial energy barrier, and increase movability.

Features of the Designed Nanoparticles

- High mobility, water solubility, and uniform dispersion in the reservoir fluids;
- Alter the wettability of interfaces of oil with the fluid;
- remain stable at high temperature, pressure and salinity (194-248°F, TDS 150,000-300,000 ppm)
- Tunable chemical composition, shape, size, porosity and functionality;





- Environmentally friendly;
- Low cost.

Task 1. Development of Nanoparticle Enriched Surfactant for EOR

1.1 Synthesis of Porous Silica Nanoparticles. The porous silica nanoparticle will be synthesized using reverse microemulsion method. a)porosity; b) surface chemical groups; and c) sizes, through changing microemulsion composition, reaction time, and post-coating chemicals.

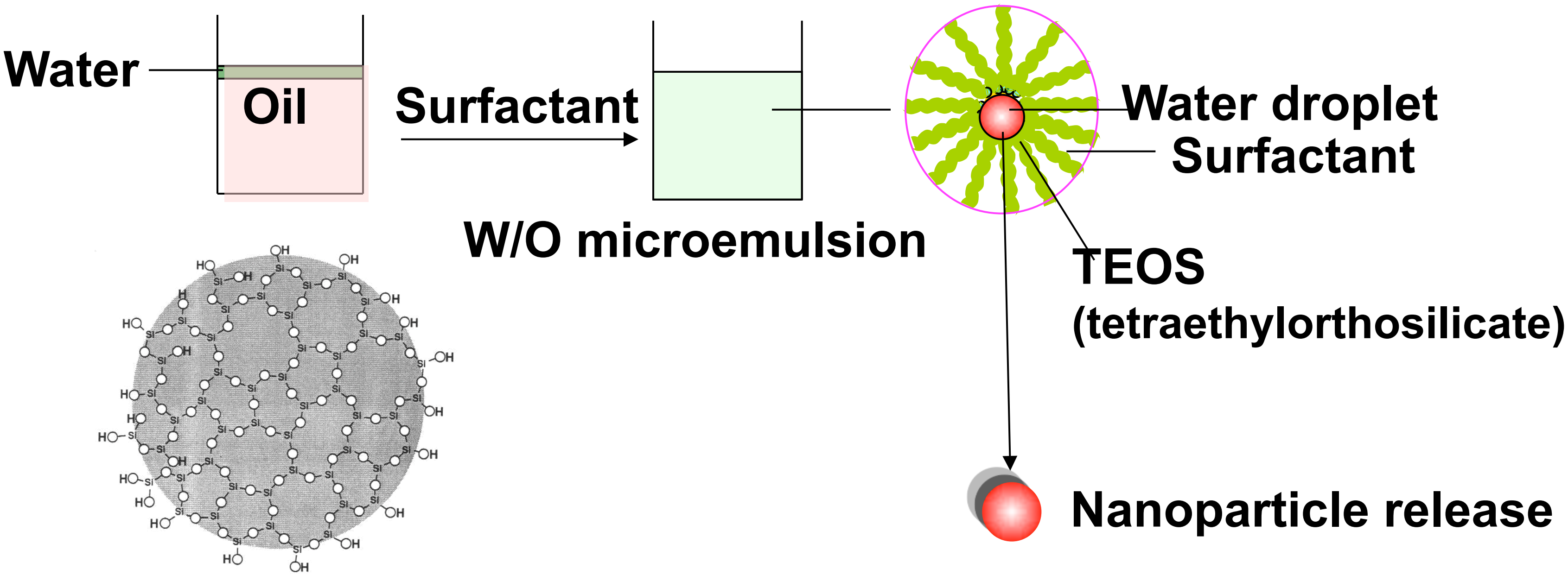
1.2 Synthesis of Non-porous Silica Nanoparticles. The Sőber method followed heating treatment will be utilized to make non-porous silica nanoparticles.

1.3 Synthesis of carbon nanoparticles. a) Carbon containing molecules and oxidative agent stoichiometry; b) Different fabrication approaches including hydrothermal reaction, microwave reaction, and combustion; c) Reaction temperature; and d) Reaction time.

1.4 Integration of Surfactants to Nanoparticles. Doping surfactants inside porous silica nanoparticles and adhering surfactant onto the particle surface.

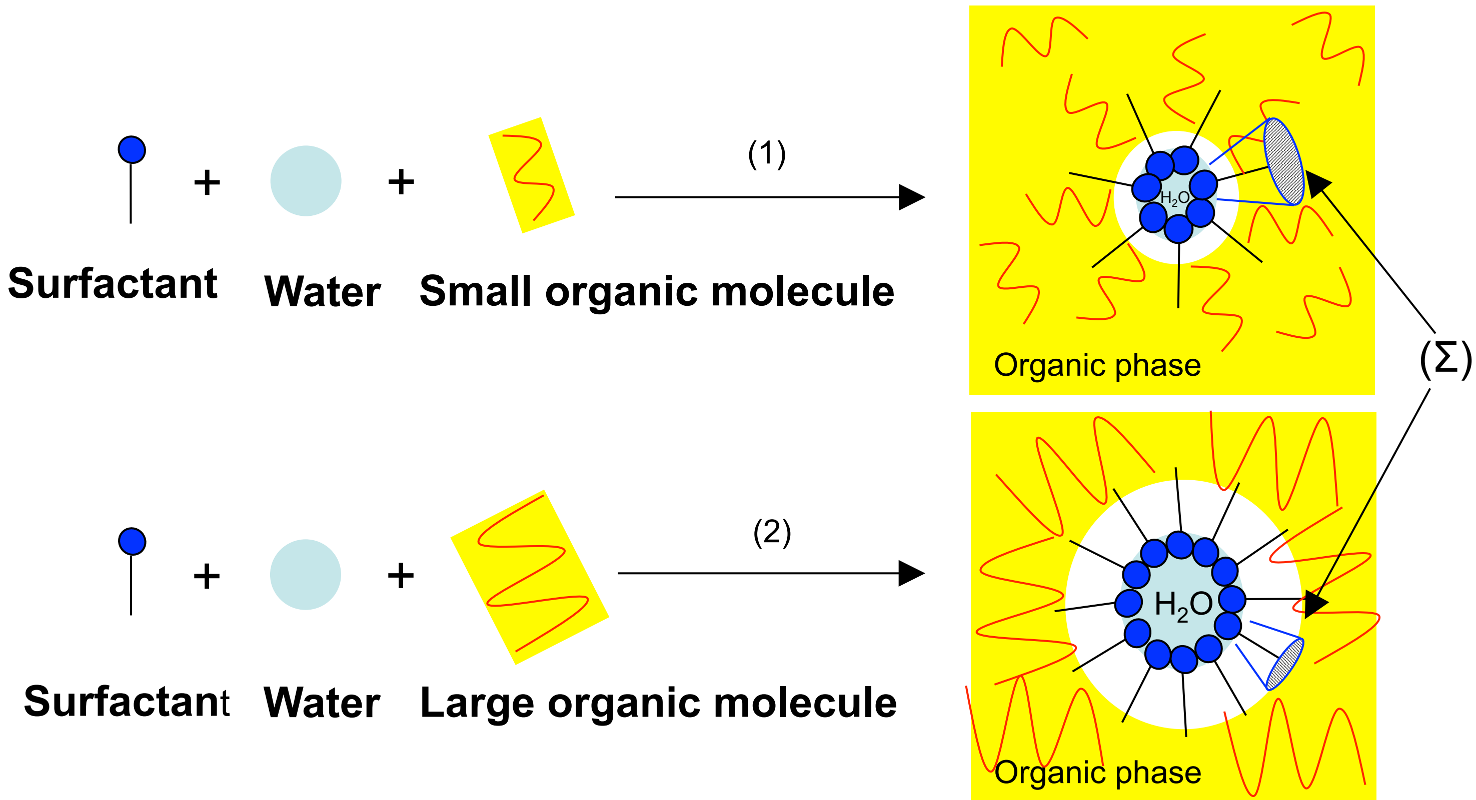
Synthesis of Silica Nanoparticles

Reverse microemulsion method

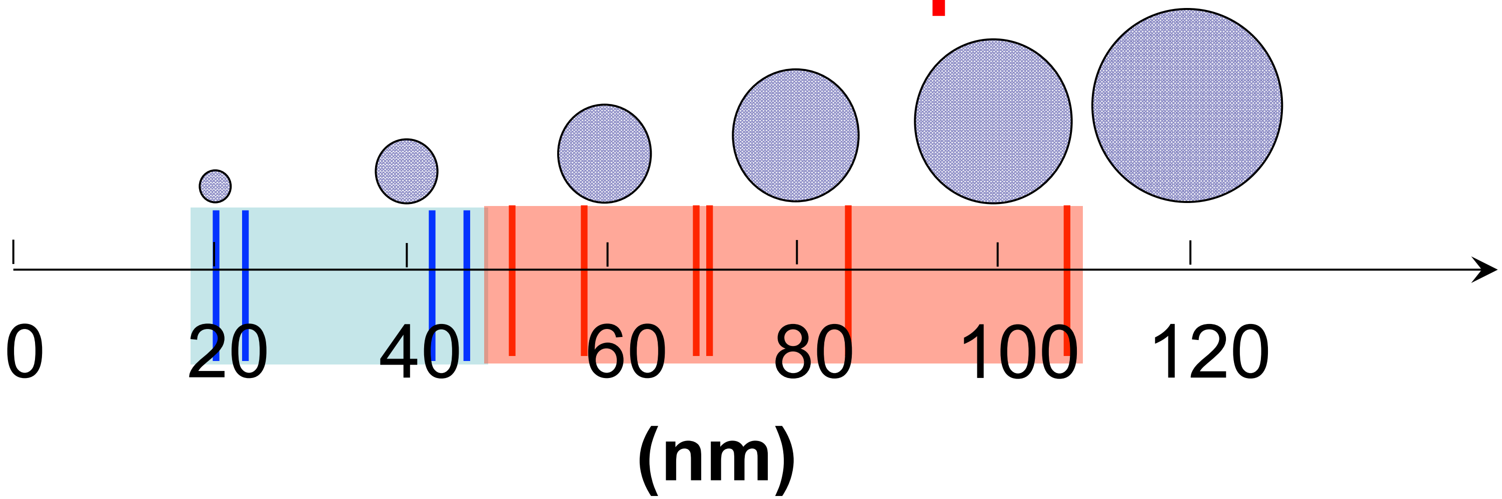


Silica network structure

Manipulation of Silica Nanoparticle Sizes by Varying organic solvents



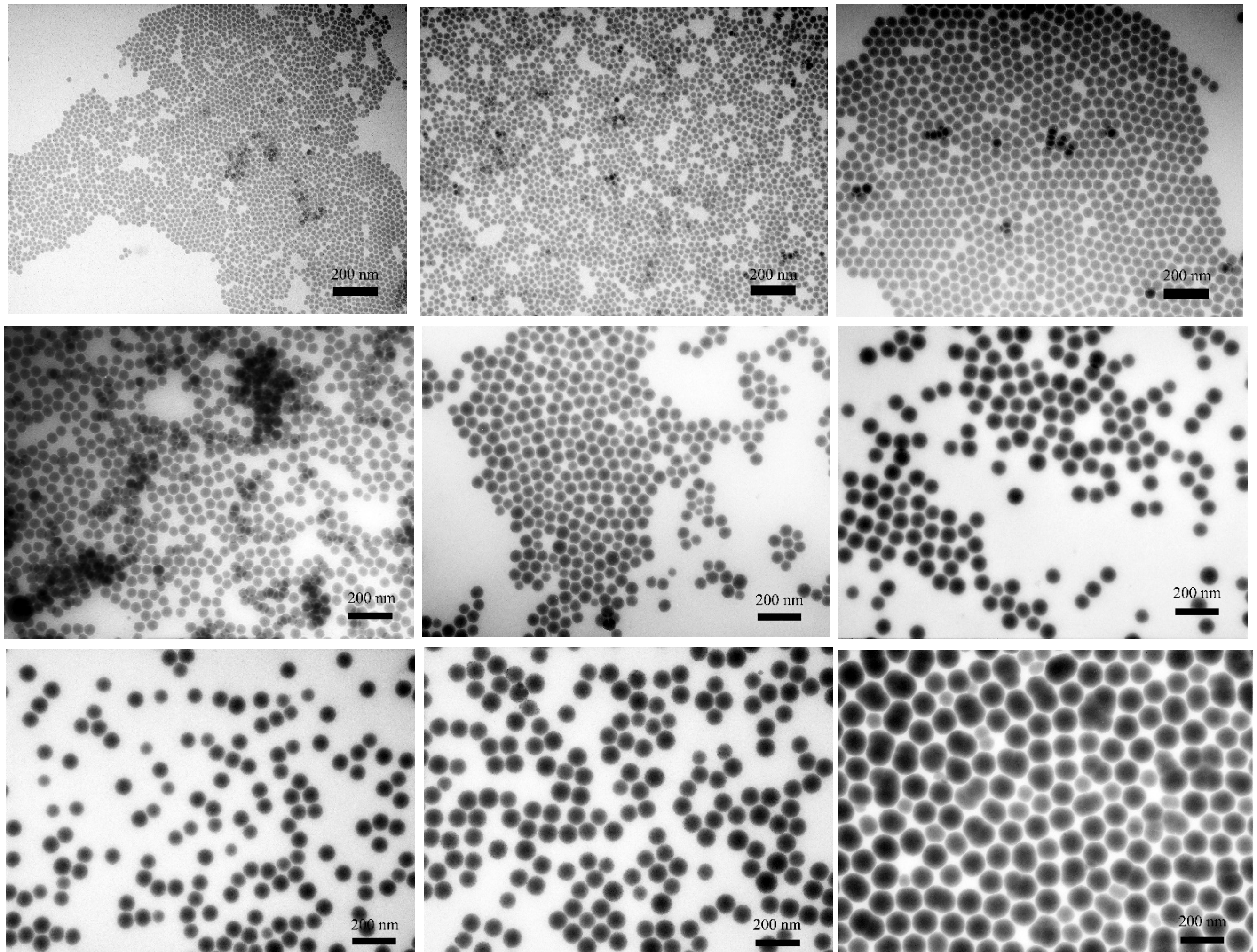
Manipulation of the Size of Silica NPs on a Continuous Spectrum



Variable on continuous range but not discrete

Y. Jin, S. Lohstreter, D. Pierce, J. Parisien, M.Wu, C. Hall, J. Zhao, *Chem. Mater.* 2008

Manipulation of Silica Nanoparticle Sizes



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Task 2 – Surfactant Screening and Nanoparticle-Surfactant Interactions

2.1 Pre-screening Compatibility Test. Brine compatibility test is a fast and effective method to identify favorable surfactant formulations.

2.2 Phase Behavior, Optimum Solubilization Ratio and Salinity. Winsor phase behavior method will be performed using different surfactant solutions, Bakken crude oil and pure hydrocarbon (i.e., decane).

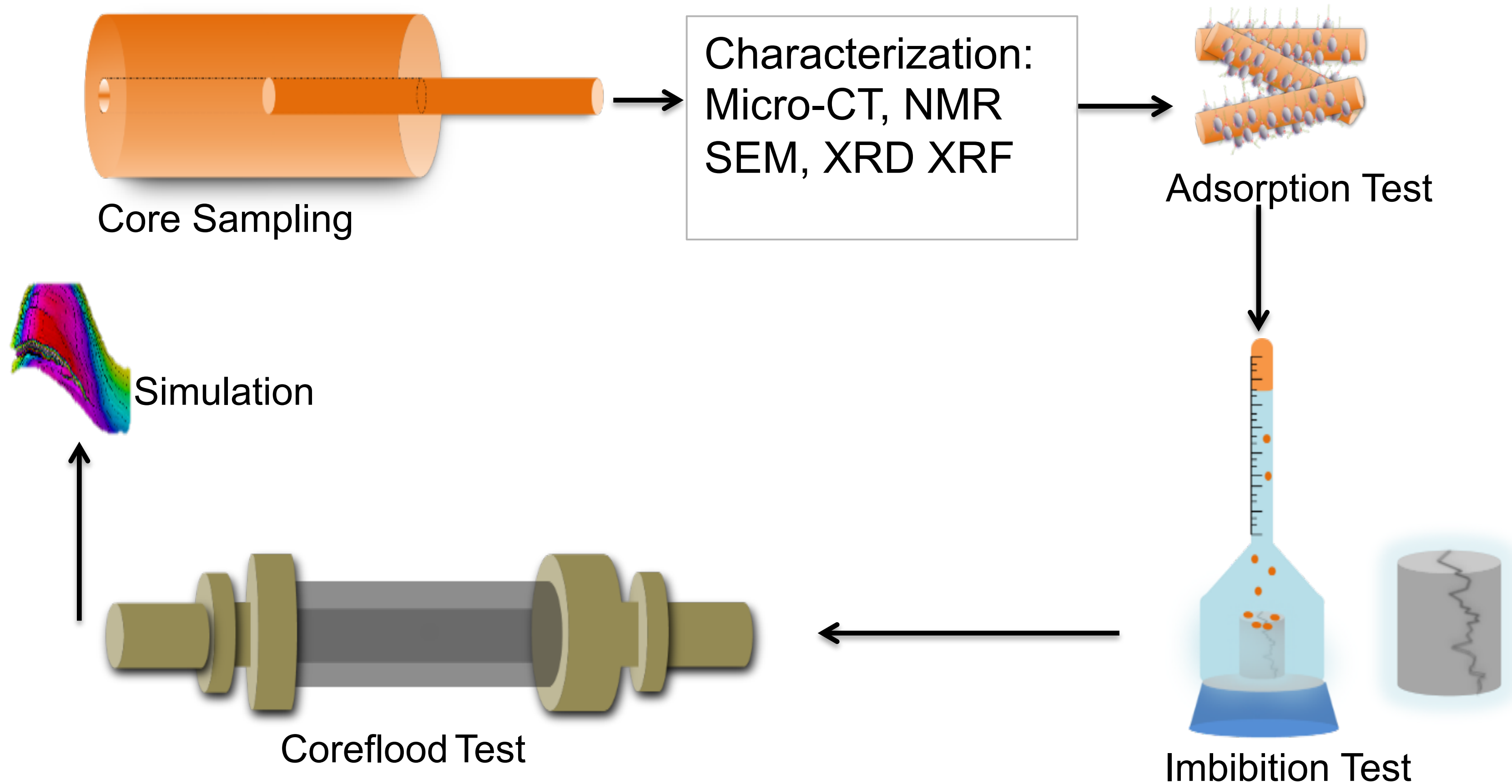
2.3 Interfacial Tension (IFT) Measurement. IFT between Bakken crude oil and different surfactant solutions will be performed at reservoir conditions using a spinning drop tensiometer as a supplement of screening surfactants.

2.4 Critical Micelle Concentration (CMC) Measurement. The CMC concentration corresponds to the point where the surfactant first shows the lowest surface tension.

Tentative List of Surfactants to be Used in Screening

Surfactant	Type
dodecyl trimethyl ammonium chloride (DTAC)	anionic
octadecyl trimethyl ammonium chloride (OTAC)	anionic
Sodium dodecylbenzene sulfonate	anionic
Sodium laureth sulfate, SLS	anionic
Sodium dodecyl sulfate,SDS	anionic
Alkylaryl Sulfonates XOF-25S	anionic
Alkylaryl Sulfonates XOF-25S XOF-30S	anionic
Isotridecanol (Exxal 13 TDA)	anionic
Isotridecanol (Marlipal™)	anionic
Guerbet (Isofol® 12)	anionic
Guerbet (Isofol® 14T)	anionic
(Isalchem™ 145)	anionic
(Isalchem™ 123)	anionic
Safol® 23	anionic
Neodol®	anionic
Internal olefin sulfonate	anionic
Sulfonic acid of Alkylate A268	anionic
alkyl alcohol amine polyoxyethylene ether	nonionic
alkyl ethoxylate (AEO-7)	nonionic
SURFONIC® L-series surfactants	nonionic
Ethoxylated Alcohols	nonionic
dodecyltrimethylammonium bromide	cationic
Ethoxylated tallow amines	cationic
coco amido propyl betaine	amphoteric
Dimethyl amine oxide	amphoteric

Task 3: Characterization of Bakken Core Samples



Schematic diagram of rock characterization procedures

Characterization

•*3.1 Petrographic characteristics.* The integrated analysis of minero-petrographical, physical parameters of the rocks can substantially reduce the uncertainty and difficulty in the data interpretation of EOR experimental study.

•*3.2 Rock Characterization Using NMR and Micro-CT Techniques.* The SEM images will be analyzed in conjunction with results from an advanced Oxford Geospec2 NMR core analyzer (with Green Imaging Technologies Imaging GIT Imaging System) at the UND lab. An advanced high-resolution x-ray micro-CT system at the University of Minnesota will be utilized together with NMR to thoroughly analyze images.

Task 4. Evaluation and Optimization of the Nanoparticle-surfactant Hybrid for EOR

- *4.1 Adsorption Measurements.* Adsorption of different concentrations of surfactant and nanoparticle-enriched surfactant solutions onto crushes Bakken sand grains will be measured using batch equilibrium adsorption procedure.

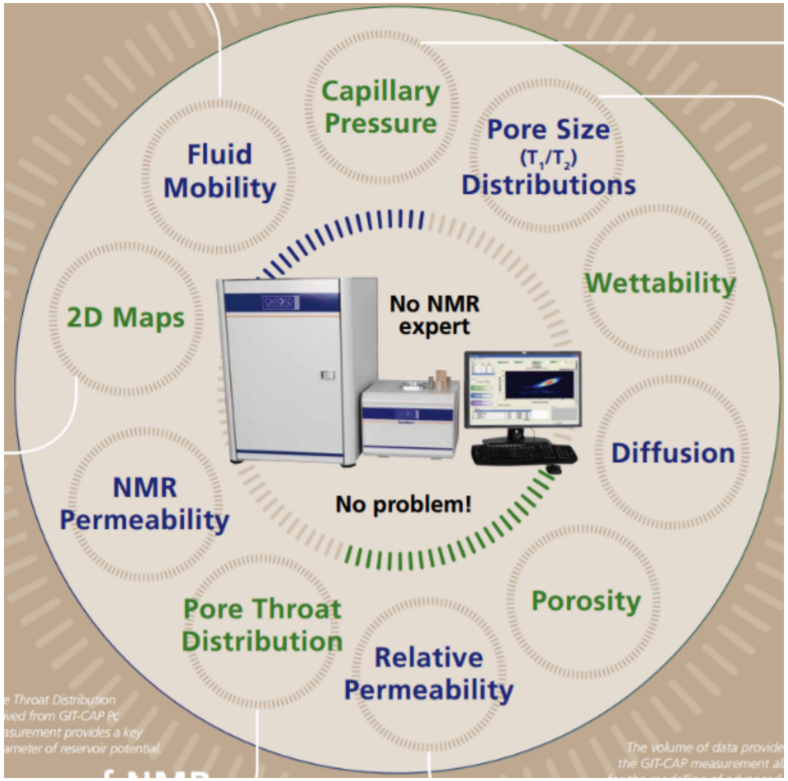
- *4.2 Oil recovery Experiments.* Effect of artificial fractures on oil recovery will be investigated by creating fractures in some of core plugs. Four of the core plugs will be fractured with different orientations using a saw, and assembled with polyoxymethylene (POM) spacers to maintain a constant fracture aperture of 1 mm.
- *4.2.1.Imbibition Tests.*
- *4.2.2 Coreflood experiment*.

- *4.3 Reservoir Simulation of Imbibition and Oil Displacement Processes.* A reservoir simulator developed by InPetro Technologies Inc. will be used in this study.

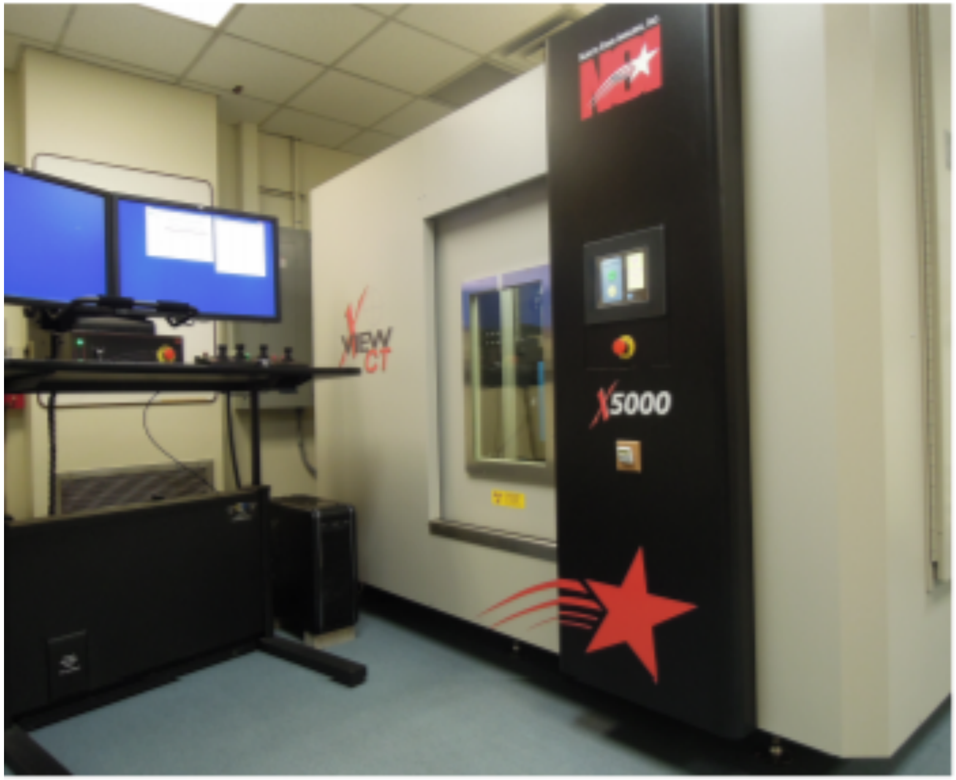
Facility for Characterization of Nanoparticles

Surface Area Analyzer, Particle size analyzer, and SEM
Zhao's Nanochemistry Lab at UND.

Facility for Characterization of Bakken Core Samples



Core Analyzer - GeoSpec2+ - Oxford Instruments



X-ray CT Lab, University of Minnesota

Newly Purchased Vinci EOR Core Flood System and Vinci Visual Fluid-Eval PVT System in Petroleum Engineering at UND

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Collaborative Energy Complex

Oct. 14, 2016 source: www.hess.com

Willison Laird Core and Sampling Library

Our Industriel Partner

- EOG Resources Inc. is providing Bakken crude oil samples from its North Dakota wells.

InPetro Technologies Inc. will provide software for simulation.

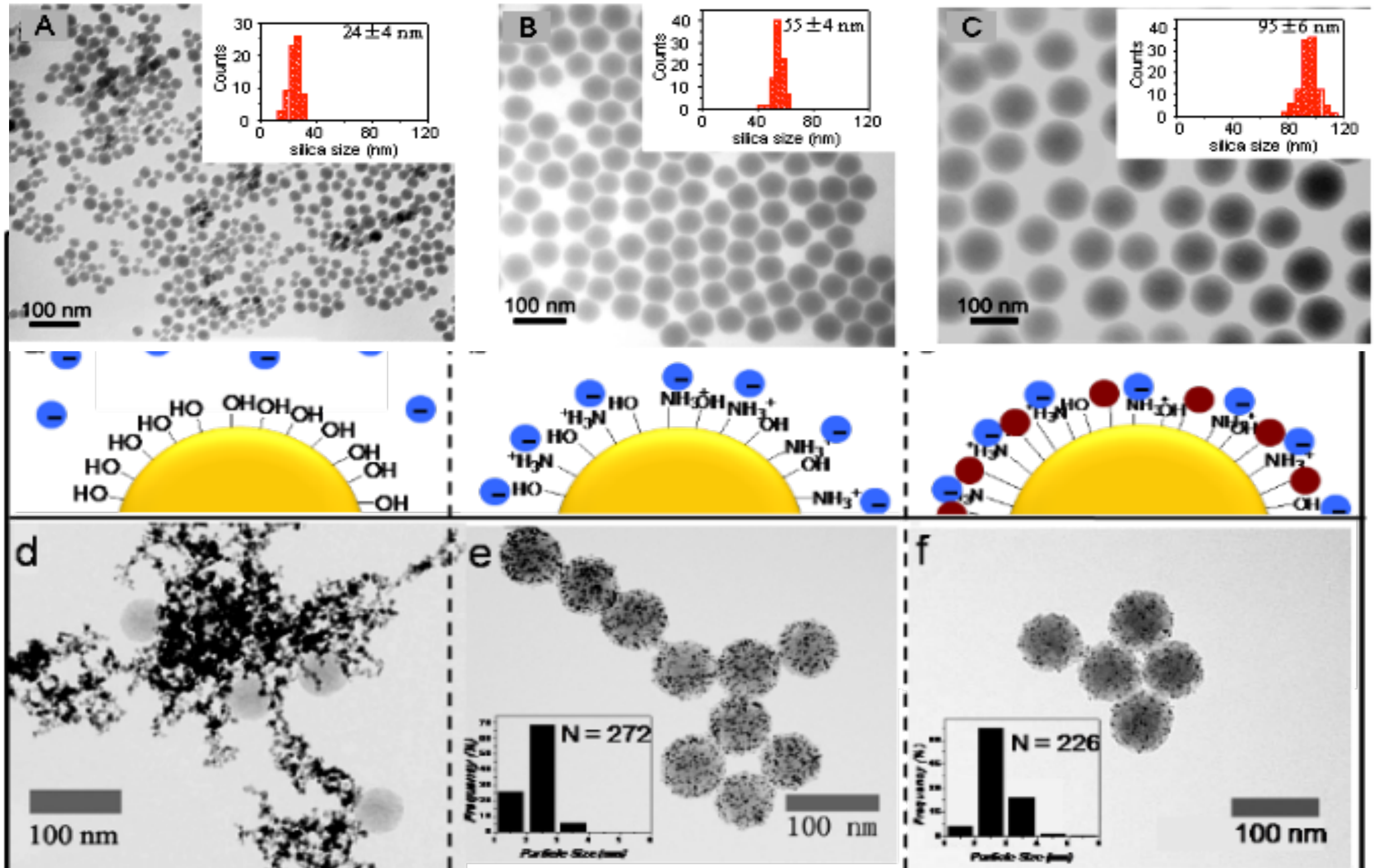
Reported Initial Study Using Nanoparticles for EOR

- Nanoparticles included Fe(III)O, CuO and NiO have been studied for carbonate reservoirs.

- Hydrides of surfactant-silica/carbon nanoparticles have not been reported for EOR.

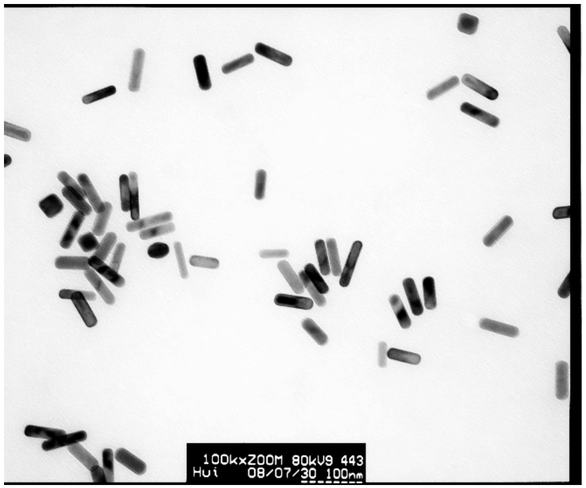
- Nanoparticles have not been used for EOR in Bakken formations.

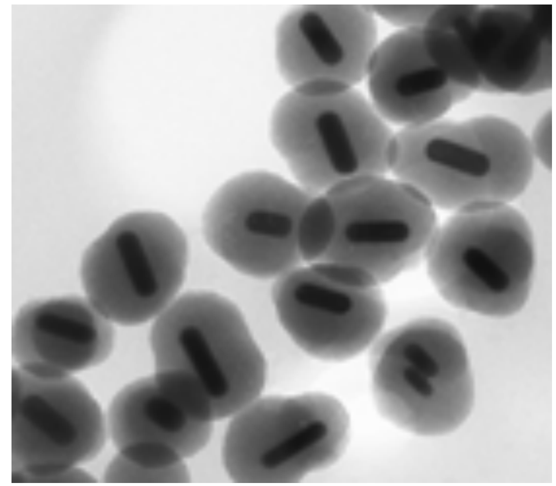
Preliminary work

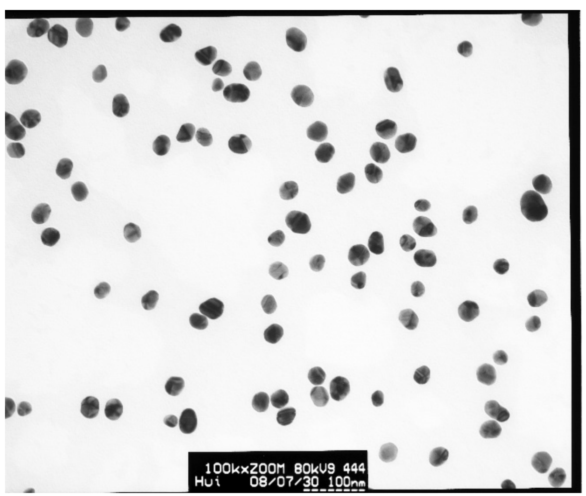


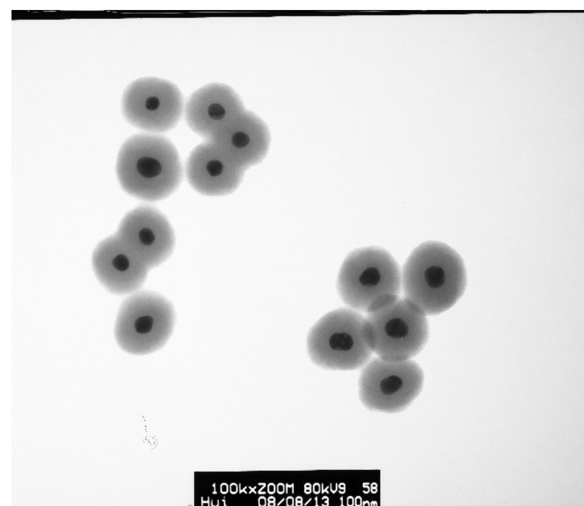
Silica-based Catalysts

Core-shell Silica-based Nanomaterials

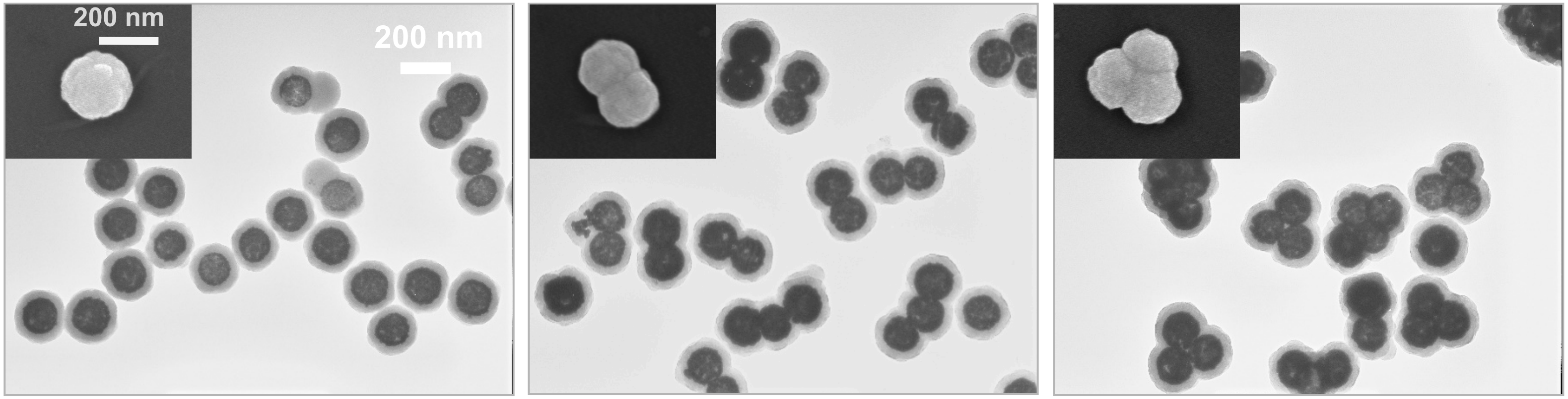


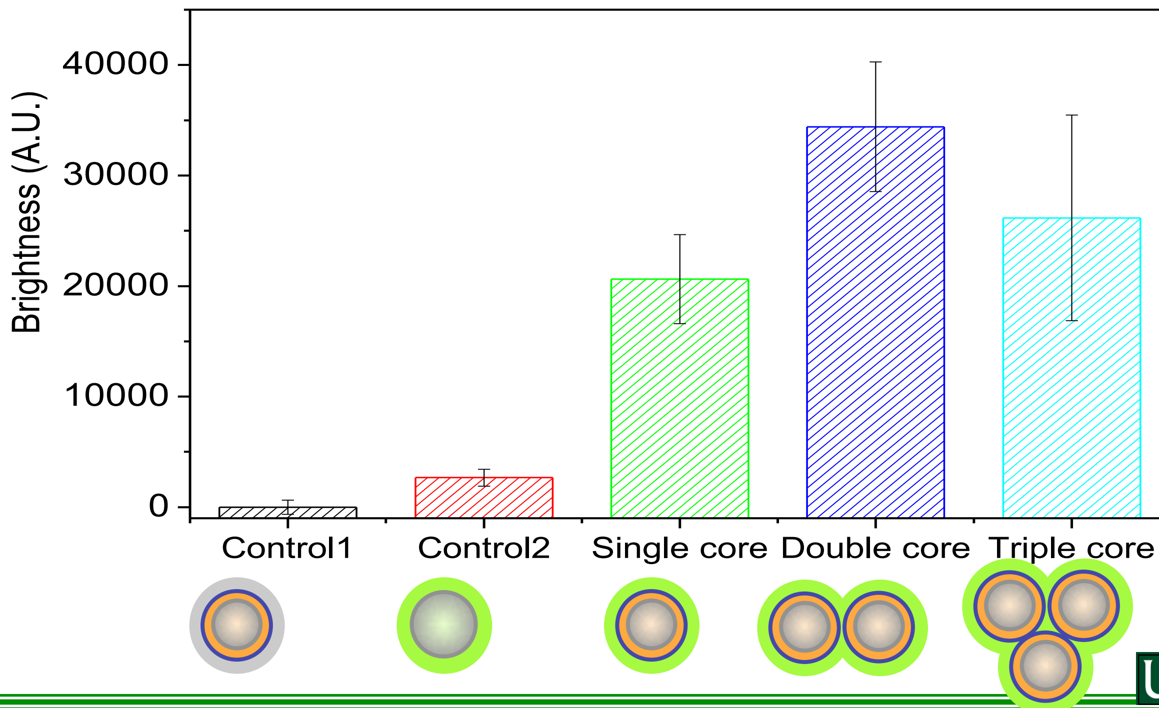




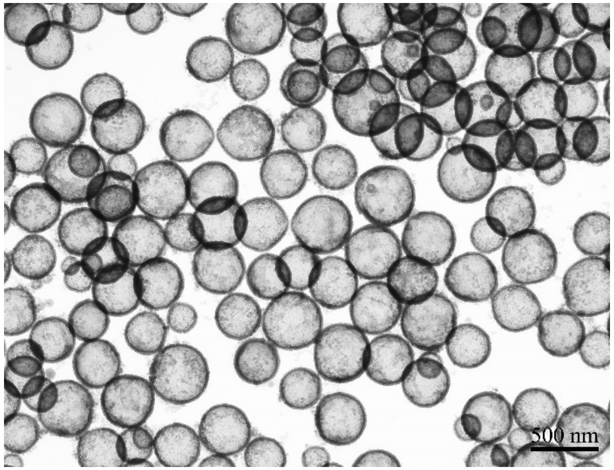


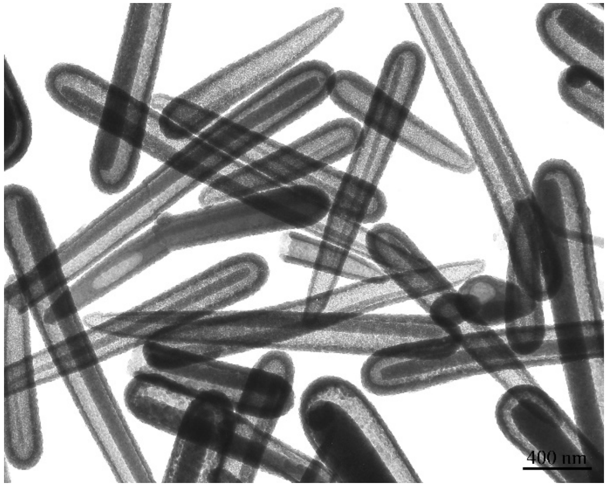
Silica Aggregates

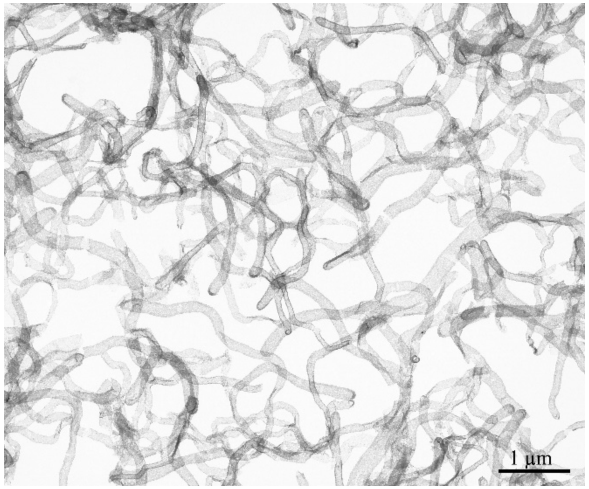




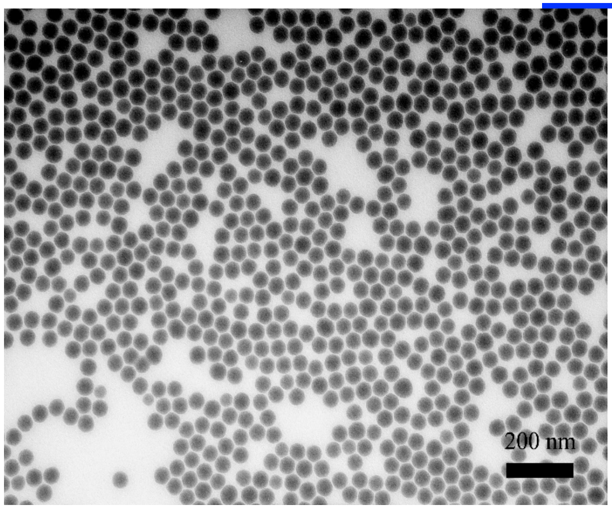
Hollow Silica Nanomaterials

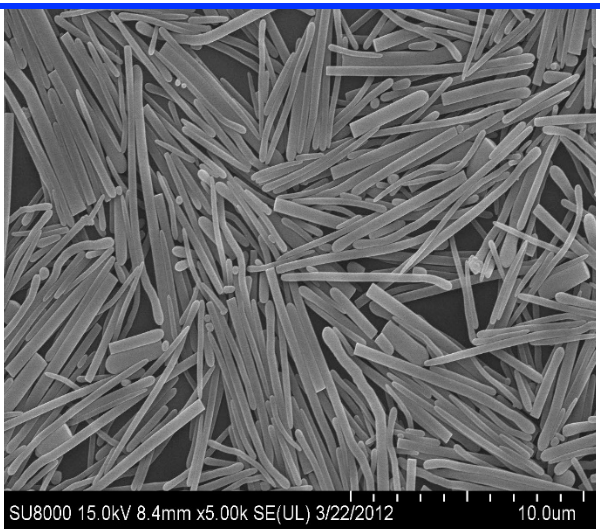


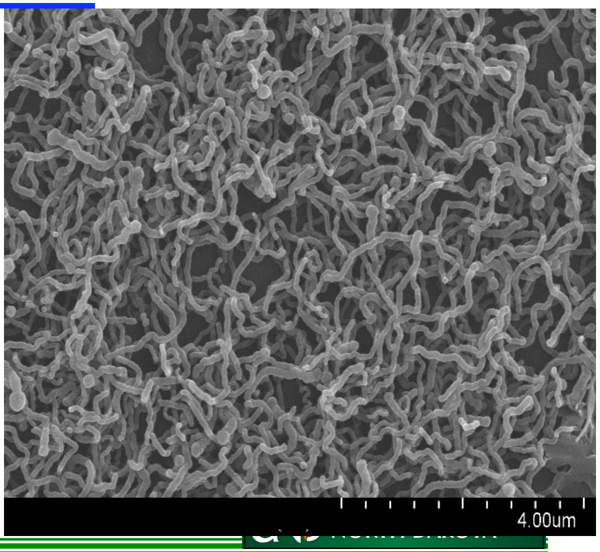




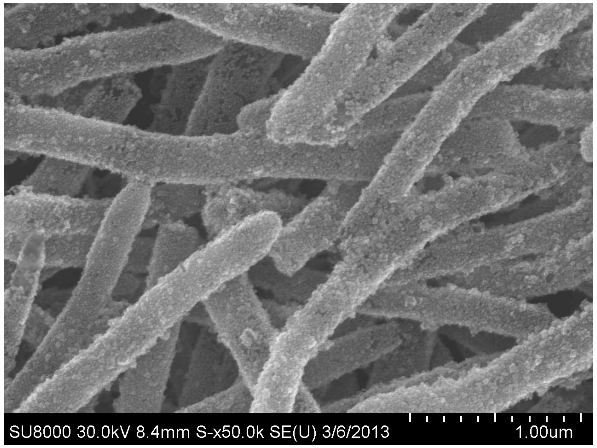
Solid Silica Nanomaterials

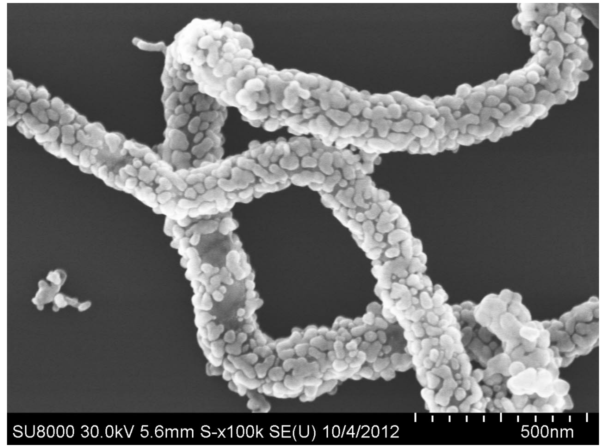


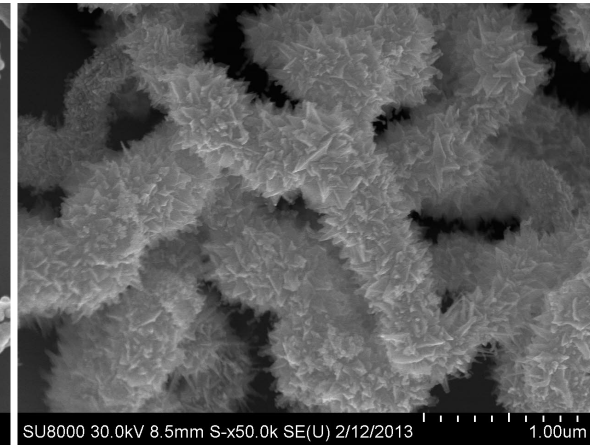




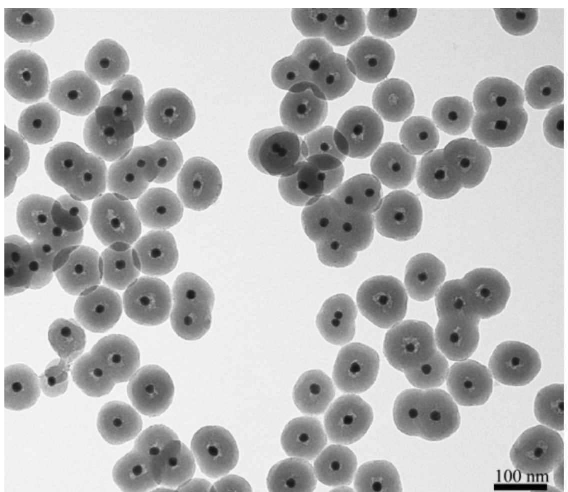
Silica-Gold Core-Shell Nanohybrid

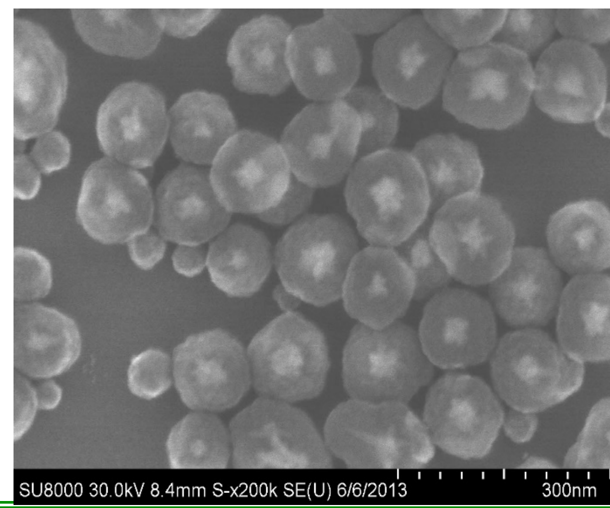




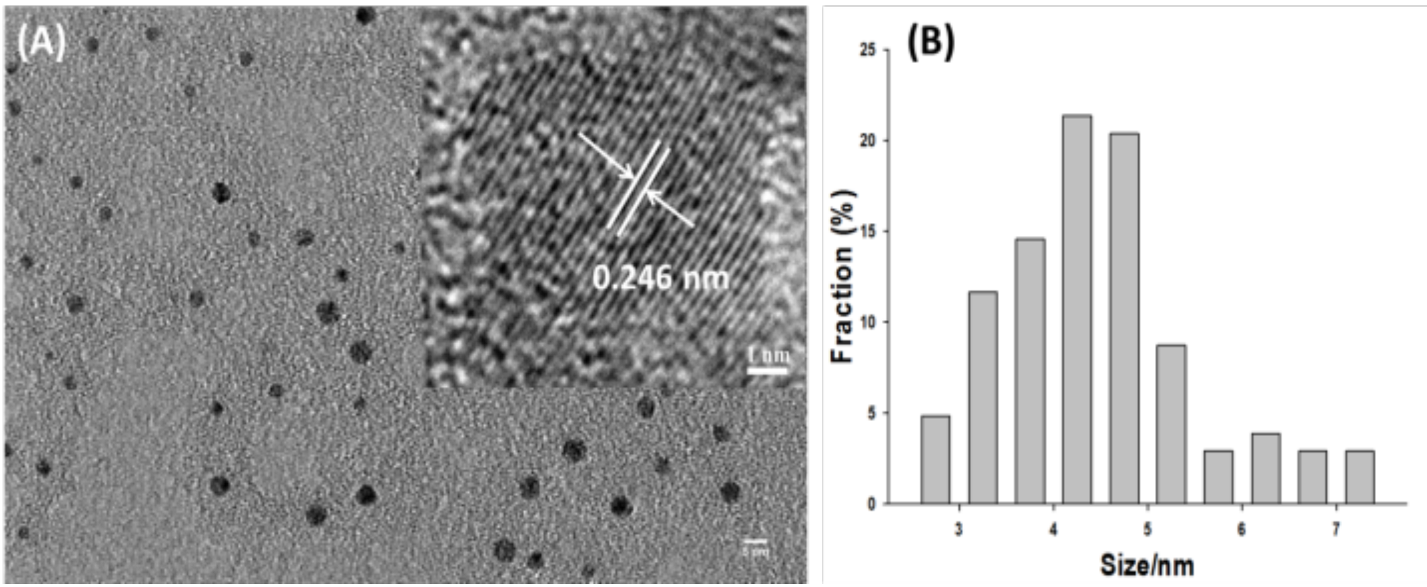


Gold-Silica Core-Shell Nanohybrid





Carbon-based Nanoparticles



(A) The HRTEM image of GQDs with a scale bar of 5 nm. Inset: A typical single GQD with the lattice parameter of 0.246 nm.
(B) The size distribution of GQDs calculated from more than 100 dots.

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Our Qualifications

Co-PI, Dr. Julia Xiaojun Zhao, Research Group

Over 70 publications, 4 issued patents in the field of development of new nanomateials.

Postdoc Researcher: Dr. Xuefei Zhang

Postdoct Researcher: Dr. Kate Zhang

Ph.D. Students:

Yuqian Xing Ph.D. candidate in nanoscience

Hana Han: Ph.D. student in nanoscience

Karen Liu Ph.D. student in nanoscience

Our Qualifications

Dr. Mann, is the Executive Director of the Institute of Energy Studies. He has been involved in multiple research projects for new technology development energy production, resulting in 215 publications.

- PI, Dr. Pu has worked on EOR for 13 years. Abundant experience in chemical, CO_2, low salinity water flooding EOR, reservoir engineering, simulation and laboratory studies
- A key member for Bell Creek Integrated EOR and CO_2 Storage Project in Plains CO_2 Reduction (PCOR) Partnership at EERC. Co-authored seven project reports for U.S. DOE on EOR subject, and 21 publications.

Dr. Michael Mann, Chemical Engineering

PI: Dr. Hui Pu, Petroleum Engineering

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Dr. Pu's research on EOR was featured in SPE JPT

Pumps pull water and oil from Daqing oil field which has long been a major testing ground for enhanced oil recovery methods. *Photo: Jiamaomimi, depositphotos.com.*

push ultimate recoveries from 40% to as high as 45%, Pu said. Adding polymer is likely to get recovery past 50%, and going to ASP holds the promise of a 60%-plus ultimate rate of recovery of the oil, he said.

Post Polymer

Polymer has its limits. Sheng, who recently wrote a book on the subject, *Modern Chemical Enhanced Oil Recovery: Theory and Practice*, said polymer can add 5% to 10% to what waterflooding could ultimately produce, and ASP could add 20% to 30%. ASP is an option when a polymer waterflood reaches its economic limit, with a water cut of about 98% in Daqing.

The six Daqing ASP tests, reported in a 2013 paper by Sheng, resulted in incremental recoveries of about 20% and significant reductions in the water cut, and led to expanded testing. "They are using ASP on a large scale now," Sheng said. There are ASP applications with more than 100 injection wells, compared to an average of 5 injectors in early tests. Mass use will depend on the cost and reduced operating issues. "There are two sides to everything," he said.

Since strong alkali is blamed for costly maintenance issues, PetroChina is seeking a substitute—a weak alkali that limits side effects without reducing EOR performance—or a breakthrough technology that allows a combination of surfactant and polymer to be as effective as ASP, Pu said.

Another method tried in the field has been carbon dioxide injection. Liu said they have had "some success" with CO_2, which is used to free oil adhering to reservoir rock and to reduce the viscosity of heavier crude.

"For 5 years we have had CO_2 flooding," he said. There is CO_2 available in Daqing because "You must separate natural gas from CO_2," which produce together around Daqing and are separated during processing, Liu said. Reinjection answers the question: "After separation, where does it (CO_2) go?"

Well by Well

PetroChina has intensively managed the huge field with the meticulous attention to detail that traditional Chinese farmers apply to their small plots.

Polymer flooding has been credited with 25% of the production at Daqing, but there is a significant human element required to match specific chemicals to the location. "They need experts with a range of expertise to make it all work together efficiently," Sheng said.

Daqing's complexity rewards attention to detail. It is a thick sandstone reservoir with large variations in rock properties from layer to layer, as well as barriers, such as fractures, leaving many pockets of oil.

In one area researchers studied the properties of 36 oil-bearing layers, with permeability ranging from 15 mD to 710 mD. The goal of that test was to target the water injection so that it flooded hard-to-penetrate layers which had been missed, despite drilling more closely spaced wells and reducing the number of producing wells per injection well. One paper described a pattern where

Benefits to North Dakota

- The short-term value can be generated by the core study and related experimental results that can be referenced in field oil production from the Bakken (pilot test).
- The long-term value to North Dakota oil industry is ultimately realized by the full commercialization and widely deployment of the technologies invented.
- May lead to oil recovery improvements, with a potential of over 1 billion barrels of incremental oil
- May prolong reservoir life, reduce operation cost and further minimize the environmental complications.
- May create additional jobs opportunities to fuel North Dakota's economy.