

Silica-based Nanoparticles: Outlook in the Enhanced Oil Recovery

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ABSTRACT

In recent years, nanotechnology has become increasingly important in the oil and gas industry's upstream sector, both in terms of perspectives and practical applications. Nanoparticles, with their exceptional properties (chemical, electrical, structural, and mechanical), are proving to be useful for freeing trapped oil. Specifically, silica-based nanoparticles (SiO₂-based-NPs) are making a positive impact on various aspects of petroleum extraction such as rheological and stabilization characteristics of drilling fluids, wettability alteration, interfacial tension (IFT) reduction, and emulsion stability improvements. This review provides a comprehensive understanding of SiO₂-based-NPs' applications in EOR and the challenges associated with their use. It covers four methods of making nanoparticles, explores how SiO₂-based-NPs involved nanofluids affect the EOR process, discusses the mechanisms behind nanoparticle-based EOR, briefly mentions how instrumentation is used in the oil and gas industry, and addresses the

challenges of using SiO₂-based nanoparticles in EOR, while also suggesting areas for future research.

1 Introduction

The potential of the exhaustion of fossil fuels has stimulated the exploration of renewable energy sources. However, the United States Energy Information Administration (U.S. EIA) predicted that global energy consumption will grow by nearly 50% by 2050 and energy demand will likely exceed what renewables can provide alone despite the increased attention and huge investments.¹ According to the U.S. EIA's International Energy Outlook 2021 (IEO2021), renewable energy will grow faster than fossil fuels, but fossil fuels will continue to be a primary energy source alongside renewables.¹ Crude oil, a liquid fossil fuel mainly composed of hydrocarbons (carbon and hydrogen compounds), is vital for energy. However, many oil fields are in decline because not all the trapped oil has been extracted due to technological limitations.²⁻⁵

The oil recovery process has three major stages: primary, secondary, and enhanced oil recovery (EOR). In the primary process, oil production depends only on the natural reservoir energy from the formation. Secondary oil recovery is a process of injecting water, gas, or both into the formation to increase and maintain the existing pressure in the reservoir.^{2, 3} However, these conventional oil recovery methods have not yet been able to fully reveal the potential of the developed oil reservoirs, resulting in the retention of over 50% of the original oil in place (OOIP).⁶ EOR refers to the process of extracting liquid hydrocarbons by methods other than the conventional utilization of reservoir energy and the implementation of reservoir repressurizing techniques involving gas and water.⁷ To increase oil recovery, various EOR techniques have been developed, including thermal methods, chemical methods, and gas methods.⁵ However, challenges

to the application of these traditional EOR techniques remain, such as low sweep efficiency, high cost, and potential formation damage.⁴ In the last decade, emerging studies on EOR have demonstrated the potential of using nanotechnologies to solve these problems, resulting in the term NanoEOR.⁸ However, the research in the NanoEOR area is still nascent and most of the studies reported to date are at the laboratory scale.⁹

The ideas and concepts of ‘nanoscience and nanotechnology’ were first talked about by physicist Richard Feynman in a presentation titled “There’s Plenty of Room at the Bottom,” at the American Physical Society meeting at Caltech on December 29, 1959.¹⁰ The term “nanotechnology” was first introduced by Professor Norio Taniguchi in a paper published in 1974 that discussed the processing of separation, consolidation, and deformation of materials by one atom or by one molecule.¹¹ So nanotechnology encompasses the capability to comprehend and manipulate matter at the nanoscale, which corresponds to dimensions ranging from approximately 1 to 100 nanometers. These nanomaterials overcome some of the limitations of bulk materials and the unique phenomena enable a wide variety of applications.

Nanoscale particles are not new in either nature or science. However, exploring the utilization of nanosized materials in the oil industry, driven by their distinct attributes such as their extremely small dimensions, exceptionally high surface-to-volume ratio, cost-effectiveness, and eco-friendliness, presents promising new avenues.¹² The petroleum industry holds great promise for the application of nanotechnology, particularly in areas such as (1) controllable delivery of surfactant and the ability to modify the wettability properties at the interfaces between oil and the flooding fluid; (2) high mobility, water solubility, stability, and even distribution within the reservoir fluids; (3) tunable chemical composition, shape, size, porosity, and functionality; (4)

environmental compatibility, aligning with eco-friendly practices; and (5) cost-effectiveness, ensuring economical feasibility. To optimize the utilization of nanoparticles, extensive research has been conducted on critical chemical and physical factors. These include the ionic composition, size, concentration, half-life, and various types of nanoparticles, all of which are examined for their impact on EOR processes.^{13, 14} For example, Sikiru et al. (2020) studied the surface ions and charges within the electric double layer in reservoir sandstone. They concluded this surface change causes strong adsorption and bonding force. Also, they determined that the addition of more negatively charged SiO₂-based-NPs into the electrolyte can add repulsion between the oil and the minerals on the sandstone surface which can favor greater oil fluid mobility.^{5, 9} The small NP size allows them to more effectively penetrate the micro- and nano-sized pores of the sandstone substrate than traditional injection fluids, which are unable to enter and effectively displace oil being locked in those pores. Also, it is known that the NPs have a higher surface-to-volume ratio, which can result in a higher magnitude of reactivity or interaction with the adjacent surfaces, enhancing the carrying properties of the nanofluid.

A significant amount of research on the topic of SiO₂-based NPS in EOR applications has been published in the last 20 years. In this review, we first give an overview of this published research before summarizing the various techniques used for SiO₂ nanoparticle synthesis techniques are summarized. The following section also elaborates on some SiO₂-based-NPs applications to EOR operations which include rock surface wettability alternation,^{12, 15-21} oil viscosity reduction,²² generate structural disjoining pressure,²³⁻²⁵ interfacial and surface tension reduction phenomena^{22, 26-28}. The major instrumental techniques used for Nano EOR research, such as Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FTIR), Dynamic Light Scattering (DLS), UV-Vis Spectrophotometry, and Fluorescence Microscopy, are

discussed for their characterization of nanomaterials and investigations of NanoEOR performance. The final part of this paper briefly covers challenges and opportunities for future applications of Si-based-NPs for EOR.

2 *Overlook of the SiO₂-based-NPs in EOR Applications*

In recent decades, numerous studies have demonstrated the significant potential of NPs in EOR, particularly SiO₂-based-NPs. Because silica (SiO₂) constitutes over 99% of SiO₂-based-NPs and is the fundamental constituent of sandstone reservoirs, these NPs are generally considered an environmentally friendly additive.²⁹ A search of the SciFinder database from 2002 to 2023 shows publications about SiO₂-based-NPs for EOR spanning 2704 journal articles, 225 review papers 144 conference proceeding papers, three dissertations, and one report. Figure 1 illustrates the number of published works by the year 2002 to 2022 and demonstrates the significant rise in publications during the last 6 years.

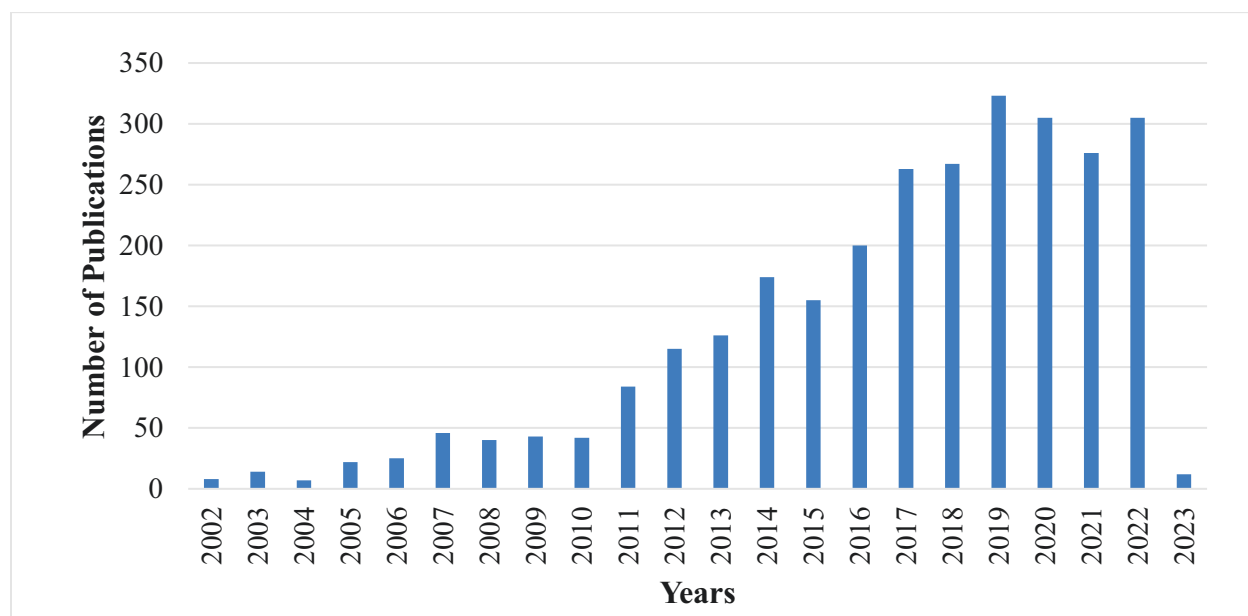


Figure 1. Numbers of publications on the use of SiO₂-based-NPs in EOR.

These publications addressed various perspectives of SiO₂ nanoparticles for EOR applications. Figure 2 illustrates these research foci and their relative prevalence in the published literature.

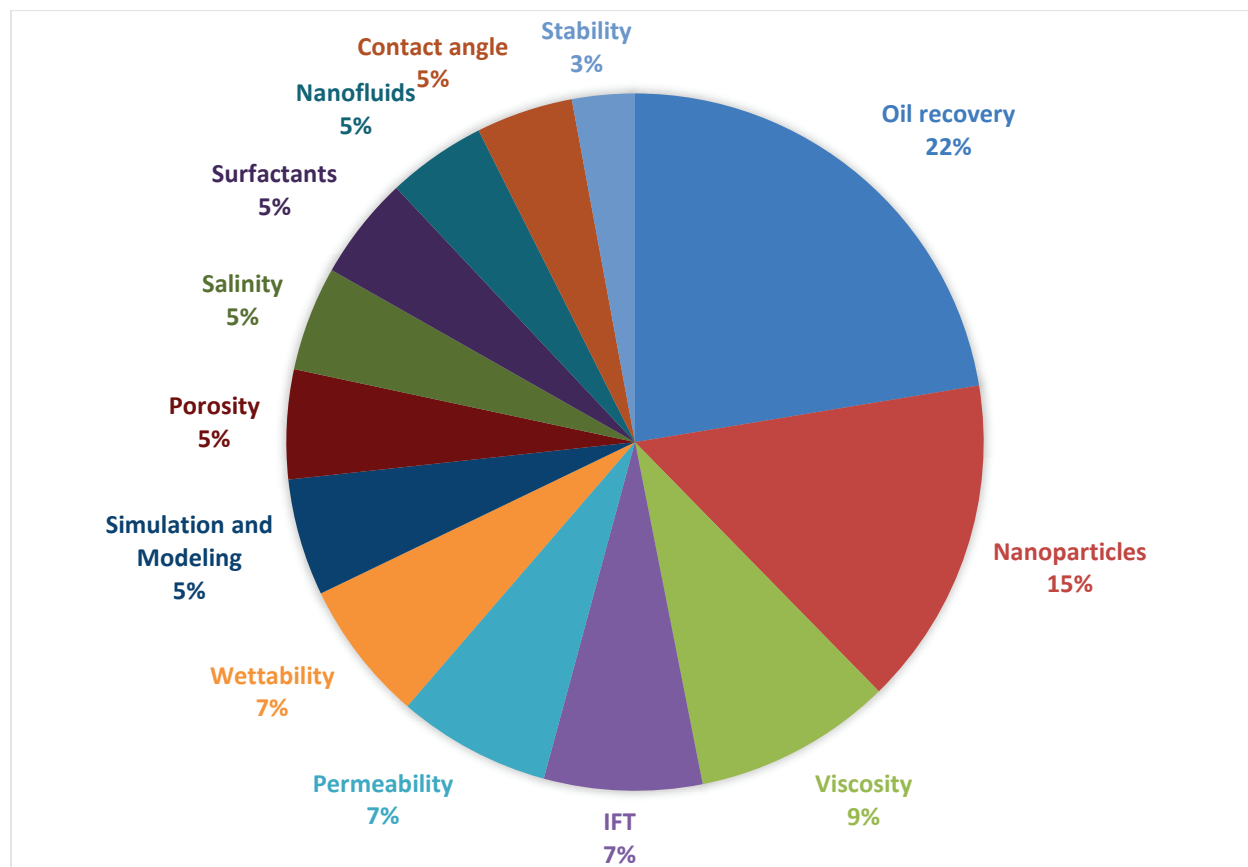


Figure 2. Prevalence of different research investigations of SiO₂-based-NPs for EOR.

The unique properties of SiO₂-based-NPs offer various advantages in EOR applications as compared to traditional chemical EOR methods. Their high surface energy and reactivity can effectively alter the wettability and IFT properties between the nanofluid and the rock, thereby enhancing the displacement of oil. Moreover, they can be modified easily through physical/chemical reactions, enabling the incorporation of various functionalities. Additionally, nanomaterials possessing magnetic properties leverage the application of an external electric or magnetic field to exert control over their mobility. To clearly understand the work published on

SiO₂ NP for EOR applications, we assembled Table 1 to summarize important categories of research being performed, including the synthetic method used for nanoparticles, EOR mechanism, experimental variables, and main observations. The work on SiO₂-based-NPs can first be separated into research on plain SiO₂-NPs and surface-functionalized SiO₂-NPs. The SiO₂-NPs alone showed excellent performance in EOR, but SiO₂-NPs naturally tend to aggregate and precipitate. The stability of NP is one of the most critical parameters for the success of EOR. This is crucial because when NPs agglomerate and increase in size, they have the potential to alter the rock properties and lead to blocking/plugging the pore throats that are generally of micron dimensions. Plain SiO₂-NPs are most likely to aggregate when they encounter brine because of their small size and high surface-to-volume ratio.³⁰ Due to this concern, NPs are typically functionalized or otherwise surface-treated to inhibit the interaction between NPs, therefore reducing the probability of aggregation. These surface treatments can be surfactants or polymers, which are coated onto SiO₂-NPs and have been shown to improve the stability and synergistic enhancement to recover more oil.^{9, 13, 14, 22, 27, 28, 30-35} The synthetic methods for SiO₂-NPs, surface functionalized SiO₂-NPs, and the preparation of the SiO₂-based nanofluid will be introduced in Section 3.

Table 1. Overview of Applications of SiO₂-based-NPs in EOR

Types of NPs	Synthetic method	EOR mechanisms	Experimental variables	Observations	Ref.
SiO ₂	Purchased	permeability, log-jamming, wettability	Nanofluid conc. 0.01, 0.05, 0.1, 0.5 wt.%	- The highest recovery factor enhancement is 13.3% - best SiO₂-NPs conc. 0.1 wt.%	²⁹
SiO ₂	Physical adsorption between surfactant and SiO ₂	Wettability, contact angle	NPs. Conc. (0-0.5 wt.%), salinity conc. (0-30 wt.%), aging time (0-5h),	0.1 wt.%, 5 h of exposure time to achieve the same θ reduction with 1 h	³¹

Types of NPs	Synthetic method	EOR mechanisms	Experimental variables	Observations	Ref.
			pressure (0-20 MPa)	exposure and a 0.5 wt.% SiO₂. - For high-concentration nanofluids, wettability alterations occurred only in the initial stages. - A minimum θ reached at 2 wt.% SiO₂, no more reductions were observed with higher concentrations.	
AEROSIL^(R) OX 50 (SiO₂ content > 99.8%)	Physical adsorption between surfactant and SiO ₂	dispersion stability, wettability, contact angle, IFT	NPs types and conc. (0.05-0.3 wt.%), temperature (25-80 °C)	- IFT was reduced by 48% with IOS19-23 O-342 coated SiO₂. - Both surface treatments and increasing NP concentration changed wettability to be water-wet.	³³
NiO/SiO₂ 0-D Janus, SiO₂	Stöber	IFT, contact angle, wettability, rheological behaviors	NPs types, NPs conc. (10-1000 mg/L)	Decreasing IFT, Increasing capillary number (N_c), and oil recovery were observed at a very low conc. of 100 mg/L of Janus NPs	³²
SiNP-NH₂	Reverse microemulsion on SiO ₂ , chemical bonding, and physical adsorption between surfactant and SiO ₂	IFT, contact angle, wettability, imbibition, core flooding test	High salinity (15 wt.%), high temperature (65 °C)	- A possible mechanism for reducing the capillary force of oil-wet reservoirs was proposed - Using nanofluids benefits wettability alteration, IFT reduction, and increasing swept volume.	¹³
SDS/Si-NPs	Purchased SiO ₂ , physical adsorption between	viscosity, wettability, contact angle, oil sweeping mechanism	Fluid type, AEROSIL-300 NPs conc. (1.8-2.2 wt.%)	5-spot glass micromodel was used to evaluate the synergistic effects of SiO₂-NPs with SDS surfactant.	³⁵

Types of NPs	Synthetic method	EOR mechanisms	Experimental variables	Observations	Ref.
	surfactant and SiO ₂			A further 13% enhancement and delayed water breakthrough were observed with the maximum conc. of the SDS/ SiO₂-NPs (2.2 wt.%)	
Porous graphene/SiO₂, MWNT/SiO₂	Stöber	wettability, contact angle, IFT	NPs types, nanohybrid type	The graphene/SiO₂ nanohybrid effectively altered wettability from oil-wet to water-wet.	36
SiO₂		wettability, contact angle	NPs size, temperature	- Oil-wet to water-wet; best conditions 60 °C, 180 min; - Sizes of NPs did not affect wettability alteration. - The immersion period affects θ more than temperature. To further reduce θ the immersion period can be decreased by increasing temperature. - Longer contact time benefits the continuing adsorption of NPs leading to lower θ and wettability alteration.	37
SiO₂		IFT, contact angle, adhesion test	Glass wettability, brine salinity	- Alternated oil-wet to be water-wet glass, maximum salinity was 41600 ppm, highest RF was 75%. - The adhesion tests showed that more SiO₂-NPs were adsorbed on sandstone grains in the presence of high salinity due to the NPs' high surface energy.	38

Types of NPs	Synthetic method	EOR mechanisms	Experimental variables	Observations	Ref.
				Wettability alteration is the dominant mechanism in EOR by nanofluid.	
SiO₂		wettability, contact angle, imbibition	Salinity conc. (0-50000 mg/L), NPs conc. (0-1500 mg/L), rock type	- The best conditions: 50000 mg/L NaCl, 1500 mg/L NPs, Dolomite rock type. - Water-wet was significantly enhanced by increasing concentrations of NPs and electrolyte concentration.	39
SiO₂		IFT, wettability	measuring time (0-36 h), NPs conc. (0.01, 0.05, 0.07, 0.1, 5.0 wt.%)	- When NPs' conc. over 0.05 wt.% the aggregation happened and the RF decreased. - The unstable of NPs and nanofluids caused formation damage leading to a significant drop in the sweep efficiency and RF. - FE-SEM images showed irreversible damage over the water-wet surfaces and almost reversible damage over the oil-wet surfaces.	40
SiO₂ with APTS	Chemical bonding between surfactant and SiO ₂	IFT, contact angle	NPs type, NPs conc. (0.25-0.5 wt.%)	- The best conditions: functionalized SiO₂ with APTS and 0.25 wt.% NPs. - The functionalized SiO₂ decreased both the contact angle and IFT. - Functionalized SiO₂ yields greater advantages for oil recovery compared to typical SiO₂.	41

Types of NPs	Synthetic method	EOR mechanisms	Experimental variables	Observations	Ref.
				Amine-functionalized SiO₂ NPs could be more effective than typical SiO₂.	
SiO₂ with VTES and DMPA	Chemical bonding between surfactant and SiO ₂	IFT, wettability, contact angle, disjoining pressure	Base fluid type (Alkaline water, salty water, nanofluid)	- The SiO₂-NPs altered wettability to water-wet. - SiO₂-NPs had little influence on oil/water IFT. - As the structural disjoining pressure mechanism described the SiO₂-NPs can slowly separate the oil droplets from the hydrophobic surface.	42
SiO₂/TX-100	Physical adsorption between surfactant and SiO ₂	Contact angle, IFT, wettability, disjoining pressure, imbibition	Fluid type (SiO ₂ /TX-100, YX-100)	- SiO₂-NPs with TX-100 had a synergistic effect to improve oil recovery by 16%. - SiO₂-NPs with TX-100 benefit the structural disjoining pressure arising and detaching the oil drop.	34
ZnO/SiO₂ NPs/XG composite	Co-precipitation	IFT, wettability, oi/nanofluid emulsification	NPs conc. (500-2000 ppm), salinity (20 times diluted seawater)	19.28% OOIP achieved at a low salinity-polymeric nanofluid, with 2000 ppm NPs conc.	43

3 Major Methods for Preparations of SiO₂-based-NPs

Different approaches are employed for the synthesis of SiO₂-based-NPs, such as the Stöber method^{32, 36}, water-in-oil reverse microemulsion method^{13, 44}, chemical vapor deposition method (CVD)^{45, 46}, co-precipitation method⁴⁷, plasma synthesis method^{48, 49}, combustion in a diffusion flame process^{50, 51}, and pressurized carbonation^{52, 53}. Among these methods, the Stöber method, water-in-oil reverse microemulsion, CVD, and biosynthesis methods are used the most when

preparing SiO₂-based-NPs for EOR applications. Each method has advantages and limitations. The comparisons among these four methods are summarized in Table 2. Based on the different geological conditions or core samples the researchers can choose different methods to synthesize SiO₂-based-NPs with different sizes and features towards successful EOR applications. The detailed mechanisms of each synthetic method, applicable conditions, and challenges were discussed in the rest of this section.

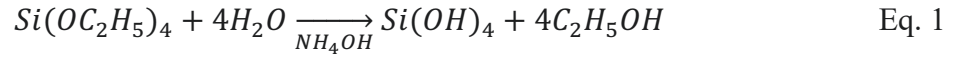
Table 2. Comparison of Different Synthesis Methods of SiO₂-based-NPs

Methods	Size (nm)	Advantages	Limitations	Ref.
Stöber	2 - 1000	Synthesis without surfactant, monodispersed particles	Particle aggregation, size range from nanometer to micrometer	54-60
Reverse Microemulsion	20 - 200	Synthesis without temperature and pressure limitations, controllable sizes	Expensive, needs surfactants, hard to purify (difficult to remove surfactants)	13, 44, 61-67
CVD	4 - 50	Minimum impurity, able to be scaled up	Particle sizes and morphology could not be controlled and required high temperature, pressure, and substrate	45, 46, 68
Biosynthesis	20 - 100	Green chemistry, using microorganisms as an environmentally friendly method	Needs to control the synthesis conditions (temperature, pH), particle sizes hard to control	43, 69, 70

3.1 Stöber Method

Currently, the most common wet chemistry synthetic method used to prepare monodispersed SiO₂-based-NPs is the Stöber method, also known as the “sol-gel method”. It was first reported by Werner Stöber and his team in 1968.⁷¹ This method, shown in Figure 3, uses tetraethylorthosilicate (TEOS) or other silicates as a silica precursor, which is hydrolyzed in a water-ethanol mixture when ammonium hydroxide is used as the catalyst (Eq. 1). After a certain reaction period and with continuous stirring, condensation of hydrolyzed monomers occurs to form the bulk silica matrix (Eq. 2).^{72, 73}

Hydrolysis:



Polycondensation:

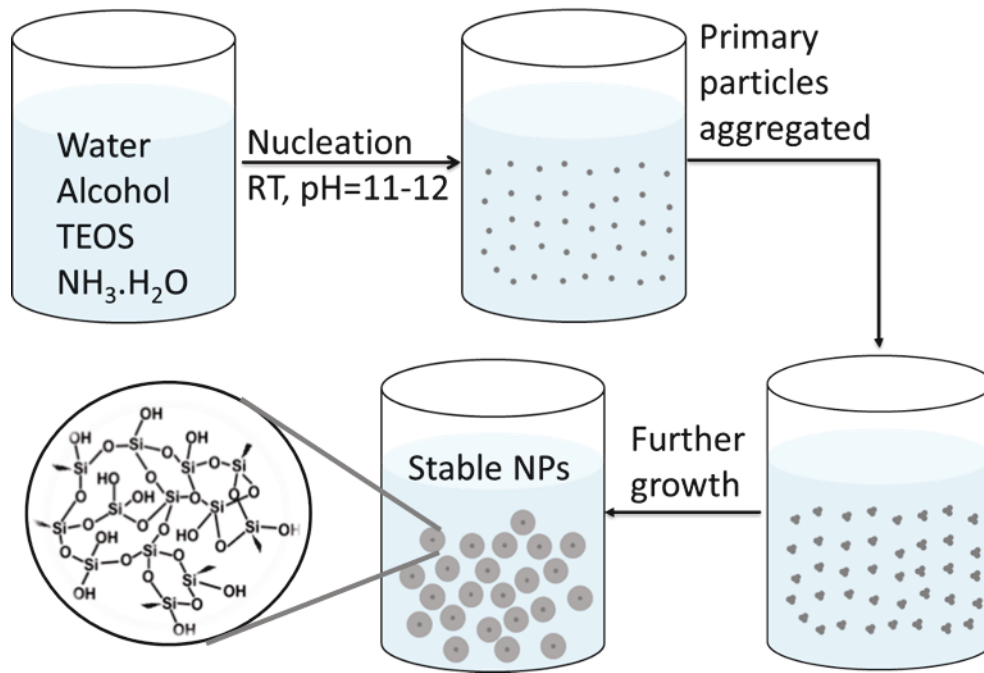
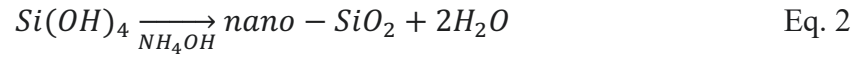


Figure 3. Schematic illustration of using the Stober method used to synthesize SiO₂-based-NPs.

The Stober method has distinct advantages when small nanoparticles are not needed. These advantages include: 1) the chemicals are cost-effective and simple; 2) the reaction occurs at low temperatures to mitigate safety risks; 3) the process produces high-purity products; and 4) the method only requires simple equipment and is easily scaled. However, a disadvantage of this method is the wide distribution in size of the SiO₂-NPs, which can range from nanometers to micrometers in diameter. For applications of NanoEOR, it is desirable to use NPs with specific

sizes and narrow size distribution. In 2019, Fernandes et al. reported investigations examining the impact of reaction parameters (water, ammonia, ethanol, and TEOS concentrations) on SiO₂-NPs sizes using the Stöber methods. As of Eq. 1 and Eq. 2, the particle sizes are influenced by TEOS hydrolysis and condensation rates: greater hydrolysis and lesser condensation result in smaller particles and vice versa.⁷⁴ In 2010, Wang et al. used high concentrations of TEOS-prepared monodispersed and uniform-sized particles.⁷⁵ In 2017, Kurdyukov et al. also used the Stöber method to synthesize SiO₂-NPs but on replacing 12.5 mol% of TEOS with [3-(methacryloyloxy) propyl]trimethoxysilane (MPTMOS), the SiO₂-NPs sizes decreased from ~ 400 to ~10 nm.⁷⁶ From the above results, the SiO₂-NPs sizes can be controlled at a certain level by changing the concentration of solvent and the types and concentrations of silicate additives.

3.2 Reverse Microemulsion Method

The reverse microemulsion method is preferred for the synthesis of small, monodimensional, and monodispersed SiO₂-NPs.^{13, 62} In this method, a water-in-oil microemulsion is prepared which is a thermodynamically stable and transparent solution of surfactant, oil, and water.⁶¹ Figure 4 shows the process of forming SiO₂ NPs by using a reverse microemulsion. A spherical micelle is formed by mixing water and a surfactant in an organic solvent (Figure. 4). Added TEOS partitions into the micelle and, through hydrolysis and condensation, forms the SiO₂-NPs in the same size and spherical shape as the original micelle. Generally, cyclohexane, *n*-hexanol, and Triton X-100 are mixed, and then added a small amount of aqueous ammonia to form the microemulsion with vigorous stirring. After that, the TEOS was added to form the SiO₂-NPs.

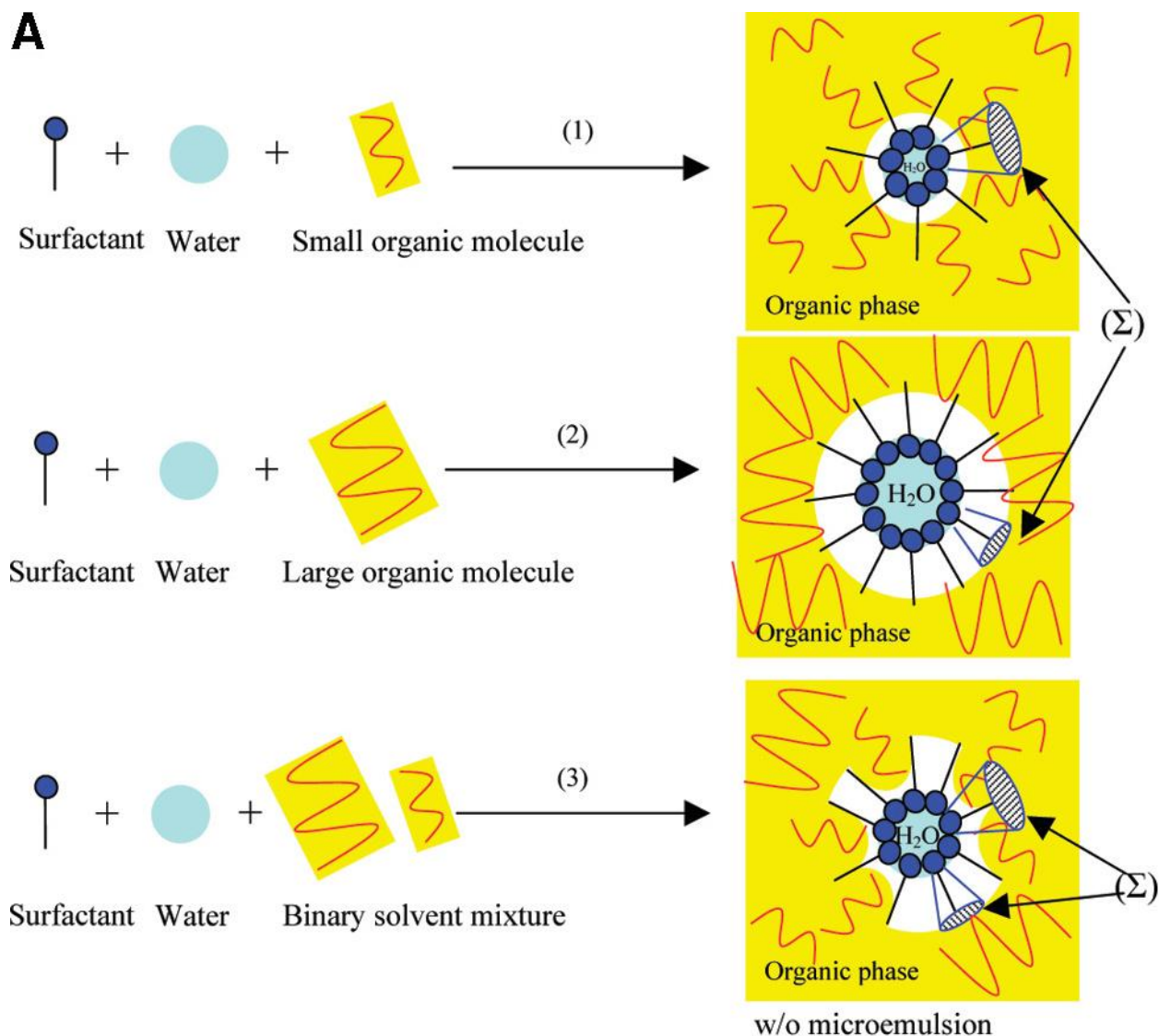


Figure 4. Mechanism of SiO₂-NPs formation in water-in-oil microemulsion.⁶² Copyright 2008 American Chemical Society.

In 2008, the method for preparing the tunable SiO₂-NPs reported by Jin et al., that the size range can be controlled between 20 to 100 nm by varying the alkane chain length of the organic solvent.⁶² They also reported other factors that can affect NP size, such as the volume ratio between water, surfactant, and cosurfactant, as well as TEOS amount. Therefore, the advantages of using the w/o microemulsion method are not only the small size and homogeneous size distribution but also the ability to easily tune the size.

3.3 Chemical Vapor Deposition (CVD)

The CVD method is utilized to produce high-purity solid materials (Table 2). In CVD, silica precursors are vaporized by high-temperature flame decomposition, which favors the nucleation process of SiO_2 -NPs. As Figure 5 shows, CVD is applied frequently with the aid of merging and depositing volatile gas molecules onto the substrate. This process occurs in the research chamber where the material is formed on the substrate and the waste gases are propelled out.⁴⁶ Sanaz Tajik et al. (2018) investigated the different concentrations of SiO_2 -graphene nanohybrids synthesized using the CVD method and their effects on EOR. The results showed that the IFT decreases via increasing the concentration of nanohybrids, and can be reduced to about half of its initial value.

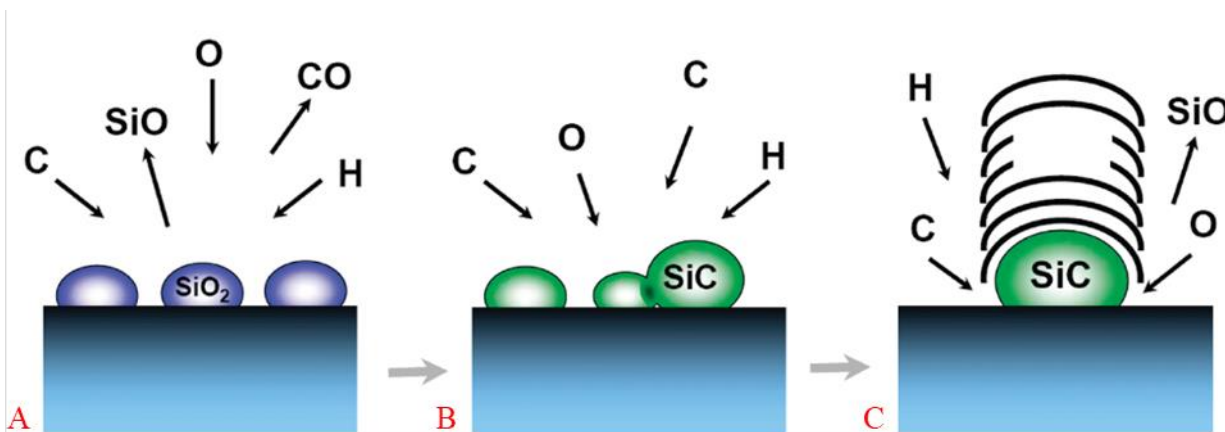


Figure 5. Schematic diagram of CVD steps involved in the carbon nanofiber formation: (A) carbothermal reaction: SiO_2 is reduced to SiC , (B) SiC nanoparticles coalesce, (C) carbon caps form on the surface of the SiC particles through precipitation and/or SiC decomposition.⁴⁶ Copyright 2009 American Chemical Society.

3.4 Biosynthesis

In the biosynthesis method, microorganisms are used to make metallic nanoparticles, which are eco-friendly. Jagar et al. (2019) developed an affordable method to create a polymer-coated

ZnO/SiO₂ nanocomposite (NC) using pomegranate seed extract. They added this NC to a low-salinity base solution to make a nanofluid for EOR. The process of making ZnO/SiO₂/xanthan NC is shown in Figure 6. When a 2,000 ppm concentration of NC was added to the low-salinity polymeric nanofluid (LPN), it resulted in a significant 19.28% increase in OOIP. This was due to reduced IFT, higher viscosity, improved emulsion stability, and a changed contact angle from 137° to 34° indicating water-wet system.

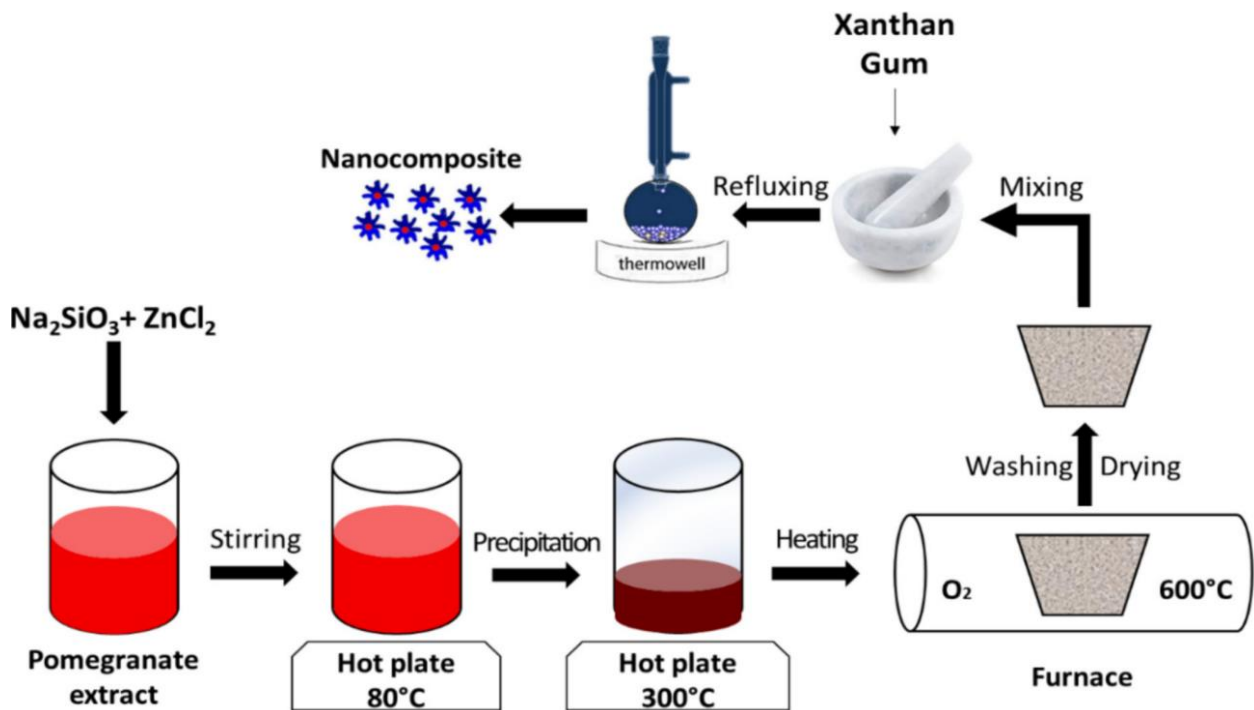


Figure 6. Schematic diagram of a one-pot biosynthesis of a polymer-coated ZnO/SiO₂ nanocomposite.⁴³ Reproduced with permission from Ref. 43. Copyright 2019 Elsevier.

3.5 Surface Functionalization of SiO₂-based-NPs for Making Nanofluids in NanoEOR Applications

As shown by Zhou et al. (2019),¹³ Zhao et al. (2018),³⁴ Ahmed et al. (2018),³³ and Al-Anssari et al. (2018)³¹ the initial step in NanoEOR is preparing nanofluids. Various nanofluids can be formulated by homogenizing SiO₂-based-NPs in base fluid (e.g. DI water or brine solution)

using techniques like ultrasonic homogenizer or magnetic stirring. In cases involving high temperature and high salinity, surfactant (Soloterra, SDS, IOS, etc.) was added to the nanofluid to supercharge the SiO₂-based-NPs and enhance the repulsion to hinder aggregation and precipitation.^{31, 33-35} The nanofluids have been extensively studied for their ability to reduce IFT, increase the viscosity of the displacement phase, and altering the wettability, which impact the capillary number and applied effectively in EOR.^{8, 14}

During the preparation of a nanofluid, there are matters about stability that need to be addressed such as promotion of uniform and stable suspension, control of NP aggregation, and minimization of chemical change during the injection. Stabilization of the SiO₂-based-NPs is the most essential step for making nanofluid and surface functionalization is the preferred method to increase the colloidal stability of these NPs. The surface modification can be done through simple physical adsorption or additional chemical reactions that involve chemical bonding to the NP surface. In physical adsorption, heterogeneous materials (surfactants) are adsorbed on the surface of the NPs due to Van der Waals forces. This method finds broad application. However, the strength and nature of the surface modification will depend on the conditions under which the nanofluid is prepared, such as pH, temperature, and concentration. Table 3 provides examples of preparing the nanofluids through physical adsorption.

Table 3. Nanofluids were prepared through the physical adsorption process.

NPs	Surfactants	Affecting Factors	Observations	Ref.
SiO ₂	SDS	NPs. conc., salinity conc., aging time, pressure	Alter oil-wet to water-wet	31
SiO ₂	Internal Olefin Sulphonates ENORDET TM	NPs types, NPs conc., temperature	With IOS ₁₉₋₂₃ -coated SiO ₂ IFT was reduced by 48%	33
SiNP-NH ₂	Soloterra 964	High salinity, high temperature	OOIP 17.23%	13

SiO₂	SDS	Fluid type, AEROSIL-300 NPs conc.	OOIP 13%	35
SiO₂	ALFOTERRA	Pressure, temperature, base fluid conc.	OOIP 20%	77

Although physical adsorption between NPs and surfactants has shown synergistic effects on oil recovery, its impact on EOR tends to be limited. Particularly for unconventional reservoirs, under high temperatures and high salinity conditions, the stability of nanoparticle-displacement systems seems to be problematic. Therefore, researchers have often turned to the chemical bonding method to prepare a more thermodynamically and kinetically stable NP-surfactant system.⁴² Table 4 illustrates examples of NP-surfactants constructed by chemical bonding.

Table 4. Nanofluids were prepared through chemical bonding methods.

NPs	Surfactants	Affecting Factors	Observations	Ref.
SiO₂	VTES, DMPA	base fluid type (alkaline water, salty water, nanofluid)	Alter oil-wet to water-wet	42
SiO₂	APTS	NPs type, NPs conc.	OOIP 18%	41
SiO₂	nonionic TX-100	fluid type (SiO ₂ /TX-100, YX-100)	SiO ₂ /TX-100: OOIP 16%, TX-100: OOIP 8%	34
SiNP-NH₂	Soloterra 964	high salinity, high temperature	OOIP 17.23%	13
SiO₂	CAPHS	Brine, temperature	OOIP 10%	78

To make the NP-surfactant systems more stable, in 2019, our group published the synthesis and application of surfactant-augmented SiO₂-NPs for EOR at high temperatures and salinities.¹³ In this work, a novel nanofluid with SiO₂-NPs was first modified with APTES through chemical bonding to form SiNP-NH₂ (Figure 7A and B), and then, the SiNP-NH₂ was modified by Soloterra 964 through physical adsorption to form the Soloterra 964-augmented SiNP-NH₂ (Figure 7C). The resulting nanofluid can remain stable for over 30 days at 65 °C and 15wt.% NaCl solution without aggregation.

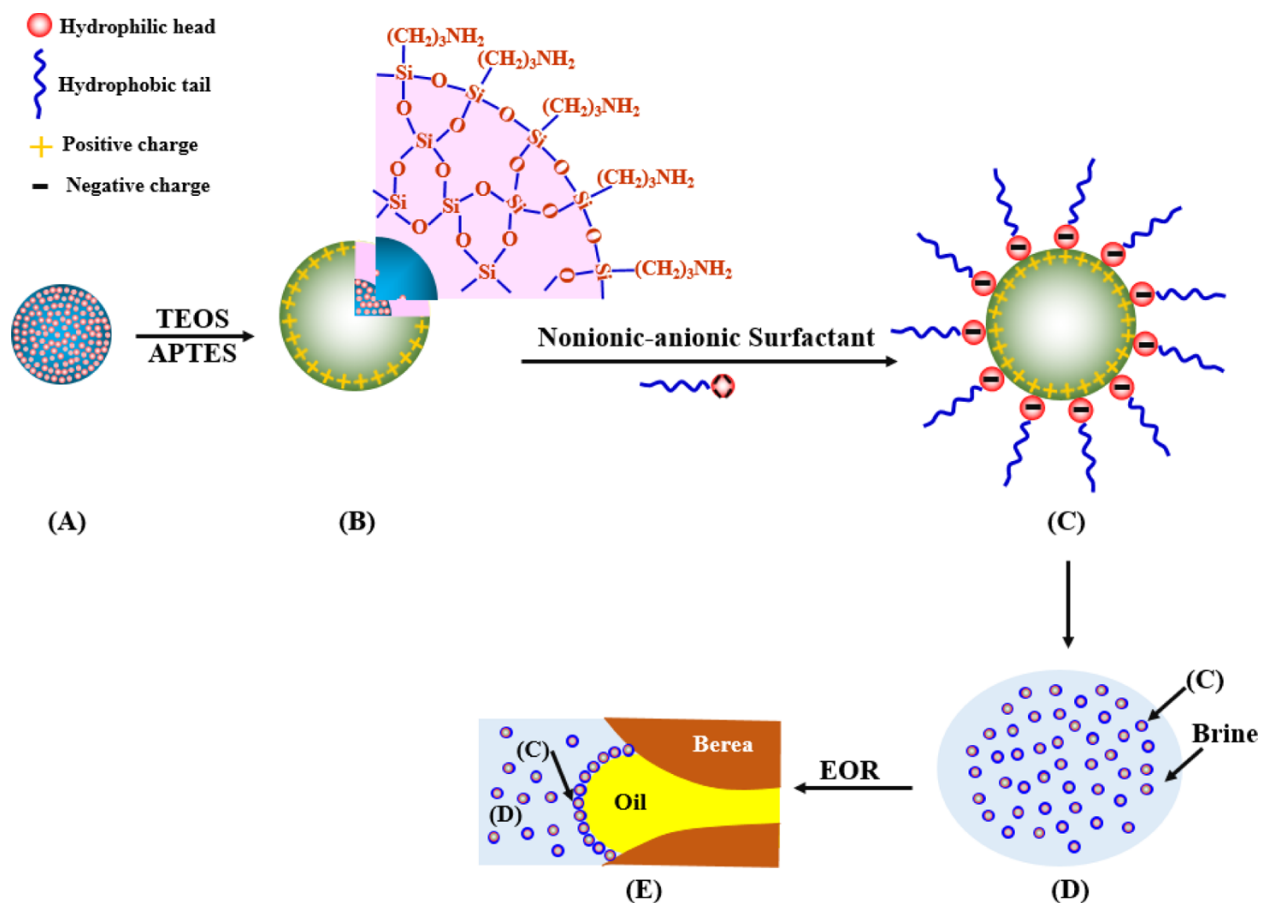


Figure 7. Synthesis of Soloterra 964-augmented SiNP-NH₂ nanofluid and applied in EOR. (A) SiO₂-NPs. (B) SiNPs-NH₂. (C) Soloterra 964-augmented SiNPs-NH₂ nanocomposite. (D) Nanofluid formed by dispersion of nanocomposite in brine. (E) Nanofluid applied in EOR.¹³ Copyright 2019 American Chemical Society.

As summarized in this section the stability of the nanofluids is influenced by various factors, including NPs characteristics, type and concentration of electrolytes in brine, surfactants, pH, NPs preparation steps, etc. More details about how the NPs' characteristics affect the EOR will be discussed in the next section of EOR mechanisms.

4 EOR Mechanisms

Understanding NanoEOR mechanisms is important for properly applying nanomaterials in specific EOR cases, and recent studies have revealed important clues to how oil, rocks, and injected

nanofluids interact. For example, in 2013 Hendraningrat et al. reported that SiO₂-NPs can be used for EOR in water-wet sandstone. They highlighted that NPs concentrations played a critical role in EOR from low permeability reservoirs.⁷⁹ Later in 2015, Roustaei et al. studied how silica nanofluids could be applied in an oil-wet carbonate reservoir and found significant potential for oil recovery.⁸⁰ In the same year, Li and colleagues investigated how hydrophilic SiO₂-NPs impact EOR through core flooding experiments.⁸¹ They concluded that oil recovery increased by injecting silica nanofluids into core samples even with low SiO₂-NPs concentrations. Multiple mechanisms have been proposed to explain these and other observations of SiO₂-NPs in EOR applications; however, a complete mechanistic understanding of NanoEOR is still in the future. Currently, our best mechanistic understanding of NanoEOR with silica NPs pertains to just a few discrete, measurable phenomena illustrated in Figure 8: (B) pore-channel plugging;⁸² (C) decreased mobility ratios of injected fluids;⁸³ (D) IFT reduction;⁸⁴ (E) wettability alternation;^{84, 85} and (F) reduction of capillary force.¹³

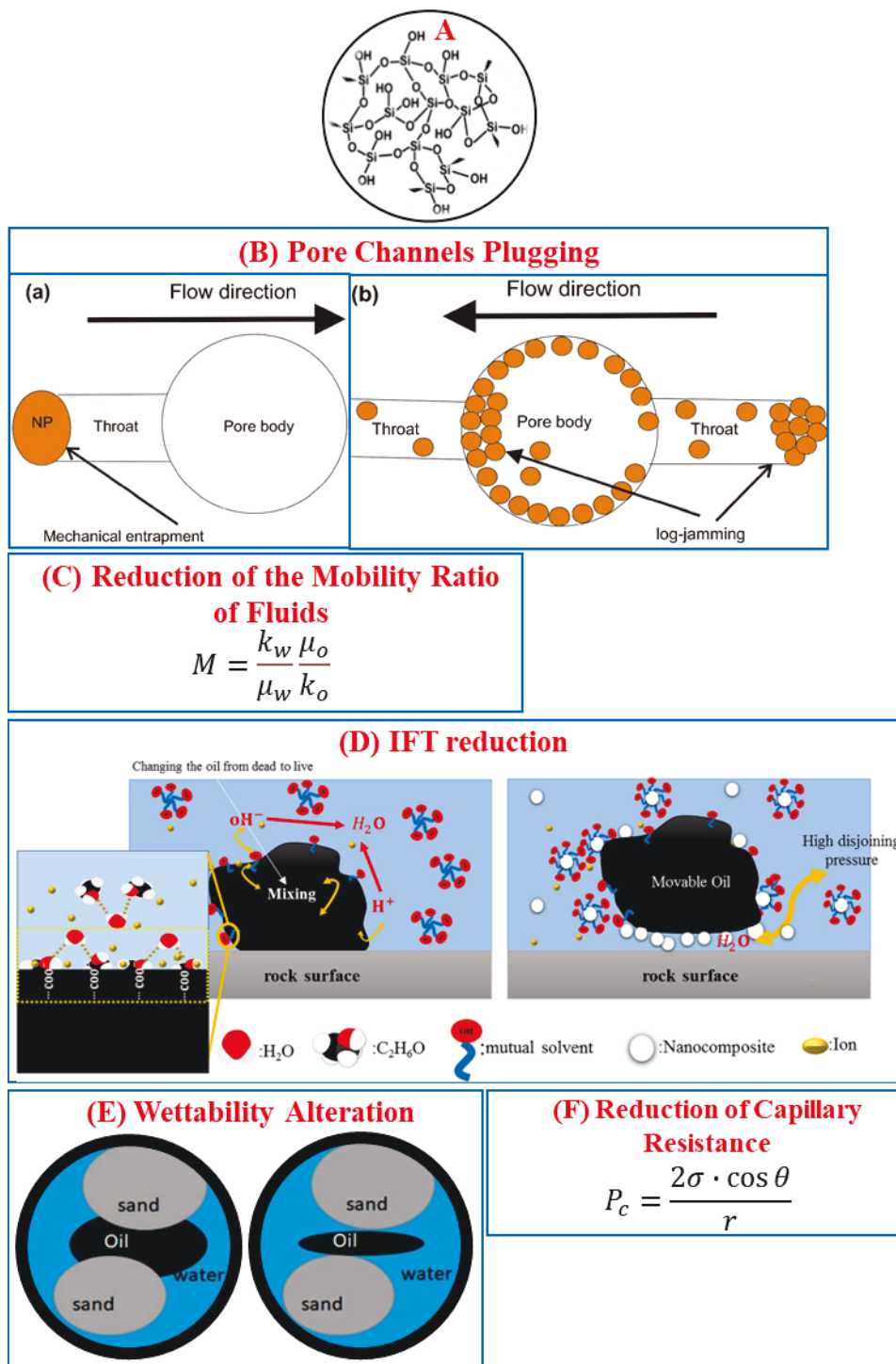


Figure 8. A schematic diagram showing (A) the chemical structure of the SiO_2 -NPs and NanoEOR mechanisms proposed for (B) pore-channel plugging;⁸² (Open access. Copyright 2021 Springer Nature) (C) decreased mobility ratios of injected fluids;⁸³ (Open access. Copyright 2020 Elsevier) (D) IFT reduction;⁸⁶ Reproduced with permission from Ref. 86. Copyright 2023 Elsevier. (E) wettability alteration;⁸⁵ (Open access. Copyright 2022 American Chemical Society) and (F) reduction of capillary force.¹³ Copyright 2019 American Chemical Society.

4.1 Mechanism of pore-channel plugging

The subsurface porous medium traps oil and has a complicated structure with throats and pores that can range in size from the nanoscale to the microscale ($0.1 - 10 \mu\text{m}$).^{87, 88} An understanding of NP movement within the subsurface porous medium is important for recovering the trapped oil, and the pore-channel plugging mechanism is often used to explain how nanoparticles blocking the pore throats and increases oil recovery. Two blocking behaviors, mechanical entrapment, and log-jamming, appear to explain the oil recovery observed to date with silica NPs. As shown in Figure 8(B-a), mechanical entrapment occurs when the NPs in the flooding fluid are larger than the pore throat. To prevent this, NPs must be smaller than the diameter of the pore throat. Log-jamming as depicted in Figure 8(B-b), results from the buildup of small NPs at throat entrances. In this scenario, NPs are small enough to enter pore channels, but as the nanofluid flows through these channels, smaller water molecules move faster than NPs, leading to NPs accumulation at the channel entrances. This log-jamming increases pressure in adjacent throat areas, forcing oil in those areas to flow out.⁸⁹ Once the oil in these adjacent pores flows away, pressure in the blocked pores drops, and the log-jamming disappears. Evidence of this log-jamming effect and its benefit to EOR has been demonstrated in several recent studies. In 2019, Ahmadi et al. used silica NPs and CaCO_3 (Bio-Ca) nanocomposite for EOR experiments and reported log-jamming as one of the likely mechanisms for enhanced condensate recovery.⁹⁰ In the same year, Guo et al. suggested that log-jamming occurs a certain time after the nanofluid injection and that most of the nanofluid traveled through those high permeable channels. The authors suggested that when log-jamming happens, it forces the injected nanofluid to change direction into the previously un-swept areas and thereby recovers additional oil.⁹¹ In 2022, Joshi et al. studied surfactant and polymer coassisted SiO_2 -NPs for EOR. They observed less log-jamming with highly

permeable cores in comparison to low-permeable cores. Additionally, they found that log-jamming caused by NPs at small pore throats is the primary factor behind reduced permeability in low-permeable cores.⁹² These publications also noted that in addition to NPs morphology (e.g. shape, size, and roughness), concentration, and zeta potential (affects NPs stability) of SiO₂-NPs are also important factors affecting whether pore-channel plugging occurs.

4.2 The mechanism for decreased mobility ratio of injected fluids

The pore-channel plugging mechanism discussed above addresses how the physical characteristics of silica NPs (e.g., size, morphology, charge, etc.) influence EOR. This section addresses how the rheological properties of both interacting fluids (the injected nanofluid and the displaced oil), as measured by their mobility ratio and viscosity differences also affect EOR. Mobility (M) is defined as fluid effective permeability (k_e) relative to viscosity (μ):⁹³

$$M = \frac{k_e}{\mu} \quad \text{Eq 3}$$

It is an important concept as it relates to the fluid flow resistance in a reservoir since low viscous fluids have high mobility. Mobility ratio is the ratio between an injecting nanofluid mobility and displaced fluid (oil) mobility. Thus, Eq (3) can be converted to the following expression:⁹⁴

$$\frac{M_w}{M_o} = \frac{k_w \mu_o}{\mu_w k_o} \quad \text{Eq 4}$$

Here, k_w is permeability to water (mD), μ_o is oil viscosity (cP), μ_w is water viscosity (cP), k_o is permeability to oil (mD). The mobility ratio is an important dimensionless number in EOR. If M is larger than 1, the nanofluid is more mobile than the oil. This creates unfavorable conditions such as water fingering, where water takes the shortest and most permeable path through the oil zone.

This results in early breakthroughs and reduced efficiency in displacing oil.⁹⁵ Recovery starts to become favorable when M approaches 1; however, recovery is most favorable when the mobility ratio is less than 1. This condition means greater oil displacement, higher sweep efficiency, and fewer fingering effects. The mobility ratio can be lowered by either decreasing the oil phase viscosity or increasing the nanofluid's viscosity.⁹⁶ SiO₂-NPs added to the flooding fluids can reduce the oil viscosity and increase the nanofluid viscosity; both of which are beneficial for improving oil recovery. The viscosity of the nanofluids can be raised by decreasing the temperature, increasing the SiO₂-NPs concentration, increasing the brine salinity, etc.⁹⁷ In 2015, Mohajeri et al. studied using nanoparticle-surfactant systems in the heavy oil EOR. They found that adding NPs to the surfactant can increase the nanofluid's viscosity and is efficient in controlling the mobility ratio.⁹⁸ Liu et al. in 2017 investigated a polymer-surfactant binary system and also found that when the viscosity of the nanofluid increased, the mobility ratio was lowered thereby enhancing sweep efficiency.⁹⁹ Recently in 2022, Ganiyeva et al. studied low salinity water injection (LSWI), and engineered water injection should best be conducted in heavy oil reservoirs. They concluded that the combination of LSW with hot fluid injection was the best approach, as it reduced the oil viscosity and enhanced the mobility ratio simultaneously. However, this conclusion was based on core flooding experiments, more investigations are required for field trials.¹⁰⁰

4.3 The mechanism for reduction of interfacial tension (IFT)

Interfacial tension (IFT) measurements in EOR applications are normally used to study the surface free energy that exists between the injecting nanofluid and displaced oil and is associated with the force of attraction between these two fluids. In general, the mobility of the oil is higher with lower IFT between the nanofluid and the oil. Lower IFT also reduces the size of the oil

droplets on the rock surface, resulting in higher mobility of the oil. A conceptual rendering of the effect IFT reduction has on EOR is drawn in Figure 8(C) and described in Eq. 5 and Eq. 6. A decrease in the oil-nanofluid IFT (σ_{ow}) means a reduction of adhesion work (W_α). The work of forming liquid droplets with a higher contact angle (θ) on a solid surface of 1 cm². This results in an easier detachment of the oil from the formation surface and improves mobilization. Young's equations⁷⁹ (Eq. 6 and Eq. 7) also show how nanofluid-rock IFT (σ_{wr}) and oil-rock IFT (σ_{or}) impact the system when the oil droplets reached equilibrium at the rock surface:

$$\sigma_{wr} = \sigma_{or} + \sigma_{ow} \cdot \cos \theta \quad \text{Eq 5}$$

$$W_\alpha = \sigma_{wr} + \sigma_{ow} - \sigma_{or} = \sigma_{ow} \cdot (1 + \cos \theta) \quad \text{Eq 6}$$

However, the IFT has the most direct impact on W_α is the oil-nanofluid IFT, σ_{ow} . Numerous studies have been conducted to determine the best nanofluid systems to use as agents for IFT reduction. Pendant drop techniques are the most commonly applied to determine the IFT between crude oil and a nanofluid.¹⁰¹ Generally, utilizing SiO₂ NPs and anionic surfactants together can reduce oil-nanofluid IFT by 70% or more than the surfactant used alone.³³ Very recently, Fatemeh et al. studied IFT reduction and concluded a nanofluid combination of 50% smart water (diluted formation water), 15% mutual solvent (ethanol/methyl ethyl ketone), and 1000 ppm of nanocomposite (KCl-SiO₂-Xanthan) led to the lowest oil-nanofluid IFT value of 3.88 mN/m under high salinity and high temperature (75 °C) conditions.⁸⁶ There has also been research exploring additions of SiO₂-NPs to the injected fluid and how these additions affect the oil-nanofluid IFT. In 2015, Adel et al. found that oil-nanofluid IFT dropped 81% by using SiO₂ nanofluids with a concentration of 0.5 wt.% compared to 61% by using Al₂O₃ nanofluids with the same concentration.¹⁰² In 2023 Younes' studied how oil-nanofluids IFT is affected by different

factors, like asphaltene content, water salinity, and SiO₂-NPs concentration. Using a drop shape analysis to perform pendant drop measurements of oil-nanofluid IFT, they found an IFT difference of about 20 mN/m between nanofluids with and without SiO₂-NPs.¹⁰³ From the extensive research conducted, the adsorption of SiO₂-NPs on either oil droplets or the rock surface alters the surface conditions of oil and water which is the primary factor for decreasing oil-nanofluid IFT. Therefore, the oil-nanofluid IFT is highly influenced by NPs concentration, decreasing as nanofluid concentration increases.

4.4 The mechanism for wettability alteration

Wettability is another common parameter used to characterize EOR processes defining how fluids interact with solid surfaces when other immiscible fluids are present.¹⁰⁴ It's especially important in NanoEOR.¹⁰⁵ Figure 8(E) illustrates different degrees of wettability in a sandstone-water-oil system. Contact angle (θ) measurements are commonly used to assess wettability, based on the value of θ wettability can be divided into three classes.¹³ As Figure 9 shows, they are water-wet ($\theta \ll 90^\circ$), oil-wet ($\theta \gg 90^\circ$), or intermediate wet ($\theta \approx 90^\circ$).¹⁰⁶ Altering the wettability from oil-wet to water-wet enhances the relative permeability of oil, facilitating oil displacement.¹⁰⁵ How this wettability change is affected by the use of nanofluids has been the subject of various mechanistic studies.

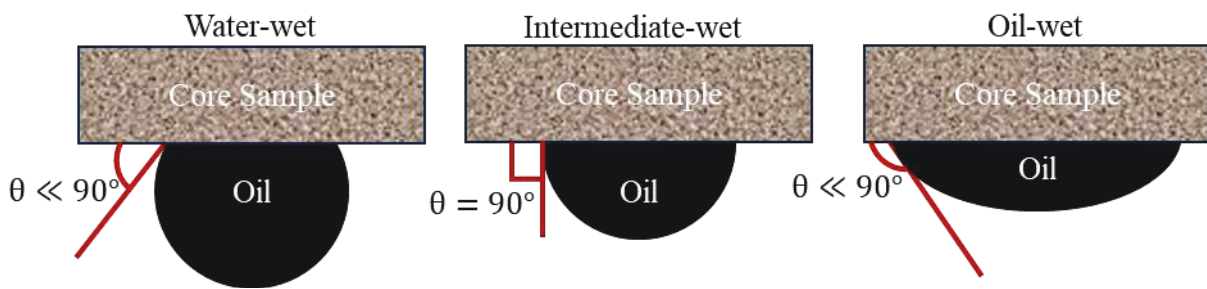


Figure 9. A schematic diagram of rock wettability conditions.

The main mechanism proposed for wettability alteration using nanofluids involves the formation of disjoining pressure.¹⁰⁷ As shown in Figure 10, the NPs tend to form a self-assembled wedge-like structure. This wedge helps the oil droplets detach from the rock surface due to the high disjoining pressure at the three-phase contact.³⁹ The disjoining pressure forces NPs to move forward toward the enclosed space which is expressed as Brownian motion and electrostatic repulsion between the nanoparticles.¹⁰⁸ At low concentrations, the Brownian motion leads to the NPs' positioning at the oil/water interface. At high concentrations, NPs interact with NPs which hinders them from moving from the bulk phase to the interface.³⁷ This has been proved by studies that when the NPs concentration increases, the force increases.¹⁰⁹ The main driving force observed is the structural disjoining pressure gradient, which pushes toward the wedge from the bulk solution. This gradient is stronger near the vertex due to nanoparticles organizing themselves in the confined wedge, aiding the nanofluid's movement toward the wedge tip as pressure increases toward the vertex.¹¹⁰ It was also observed that the spreading coefficient increases exponentially when the film thickness decreases or when there are fewer particle layers inside the film. As the film thickness decreases towards the wedge vertex, the structural disjoining pressure rises.¹¹¹ NPs play a role in promoting the spreading of nanofluid along a solid surface near the drop's three-phase contact line. They form a monolayer and create an ordered structure. When the contact angle of the aqueous phase is zero, it indicates that the nanofluid has a large surface area, allowing it to spread easily on the surface. This results from the fluid having a high surface energy of adsorption, which alters the system's wettability.¹¹²

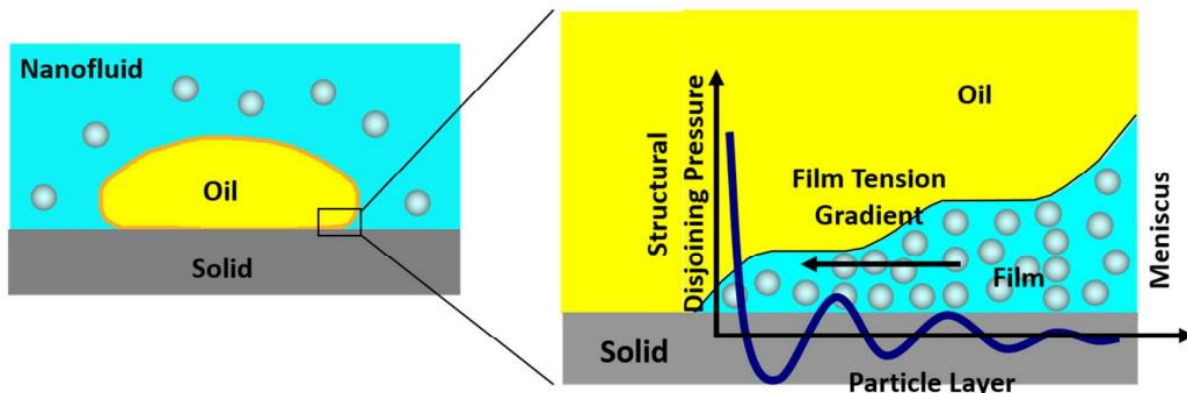


Figure 10. Disjoining pressure mechanism: nanofluid layering leads to film tension gradient and drives oil displacement.¹¹³ Copyright 2016 American Chemical Society.

Recent research revealed that SiO_2 nanofluids are effective in improving wettability. For instance, Roustaei and Bagherzadeh found that SiO_2 -NPs effectively change wettability in carbonate reservoir cores.⁸⁰ Giraldo et al. have demonstrated that NiO/SiO_2 0-D Janus nanoparticles alter wettability from oil-wet to water-wetness conditions.³² Li and his team investigated the effect of NPs concentration on wettability and found that higher concentrations led to increased water-wetness.⁸¹ Additionally, Bayat et al. demonstrated the positive impact of metal oxide nanofluids, like Al_2O_3 , TiO_2 , and SiO_2 , on altering wettability in limestone at various temperatures.¹¹⁴

4.5 Potential Mechanism for Reduction of Capillary Force

Yet another common parameter used to characterize EOR processes is capillary forces, which are responsible for trapping oil inside the pores. NPs in surfactant solutions improve fluid viscosity, change wettability, and reduce IFT. Reduced IFT makes it easier to move oil through porous media by decreasing capillary forces. This helps pull water into small pores, push oil into larger pores, and ultimately direct it to the wellbore and surface.¹¹⁵

Capillary pressure (force), P_c , represents the pressure difference in pressure at the interface between two immiscible fluids, such as oil and water, in the reservoir. The capillary pressure is given by the Young-Laplace equation (Eq. 7), where σ is the interfacial tension, r is the capillary tube radius; θ is the contact angle.¹³

$$P_c = \frac{2\sigma \cdot \cos \theta}{r} \quad \text{Eq 7}$$

While nanofluids exhibit either some or insignificant impact on IFT, nanoparticles can alter the wettability and hence decrease the capillary forces. Therefore, with the changes in capillary forces, the nanofluids invade into medium and small pores that are inaccessible to brine.¹¹⁶ This would mobilize large amounts of additional oil and improve the oil recovery. In 2017, Liu et al. named the same mechanism as the capillary displacement ratio. They discovered that the polymer-surfactant emulsion not only increased the viscosity of the aqueous phase but also raised the capillary displacement ratio. Consequently, it improved oil displacement efficiency and led to higher oil recovery.⁹⁹ In 2018, You et al. also studied the same mechanism but named the capillary forces or capillary pressure. They found that the surfactant solution changed wettability, reduced IFT in the core, and shifted capillary pressure from negative to positive. This resulted in oil mobilization through counter-imbibition, aided by capillary and gravity forces, leading to oil expulsion from both sides and the top surface of the core.¹¹⁷

5 *Instrumental Measurements Applied in NanoEOR*

A variety of analytical instruments are employed not only for characterizing NPs but also for investigating their performances for NanoEOR. Figure 11 illustrates how various instruments have been applied to three distinct categories of NanoEOR research work.

Various electron microscopies (SEM, TEM, etc.) are the most widely used methods to determine the morphology, structure, and size of the NPs used for EOR applications. Typically, if NPs are spherical and small enough in size they have demonstrated beneficial oil extraction results for low-permeable porous reservoirs.

FTIR has often been used to characterize the surface components of NP samples. By analyzing surface functional groups via their characteristic infrared absorption fingerprints, important solubility and rheological properties of NP samples have been revealed. For instance, the NPs with carboxylic groups have demonstrated excellent water dispersibility properties and FTIR is well suited to study the quality of this functionalization due to the strong carbonyl stretching bands found in the IR region.⁴¹

Dynamic light scattering (DLS) is another common method for NP size measurement, albeit as a bulk-sample distribution rather than particle-by-particle as with electron microscopy. However, other DLS information is available for assessing surface charge information via zeta potential measurements. The size distribution provided by DLS has been most often used to indicate the stability of the NP suspensions in water and the zeta potential measurement has been used to indicate their dispersibility properties. Both the stability and dispersibility of nanofluids used in NanoEOR are crucially important factors to understand because NP aggregation can occur when nanofluids are subject to high flow through high temperatures and high salinity reservoirs.⁴²

The UV-Vis spectrophotometer is a relatively low-cost method that can be used to observe the stability of the NPs by measuring the transmittances of the nanofluids at different temperatures. It gauges the intensity of light reflected from a sample and compares it to a reference material.¹¹⁸ NPs exhibit optical properties influenced by factors like size, shape, concentration, agglomeration,

and refractive index near their surface. This makes UV-Vis spectroscopy an important tool for identifying, characterizing, and investigating these materials, as well as assessing the stability of NP colloidal solutions.¹¹⁹

Atomic force microscopy (AFM) is a microscopy technique capable of providing 3D surface images at high magnification. It can be used to study the impact of irreversibly adsorbed NPs on the surface and reveal the surface roughness. The advantages of using AFM include (1) no need for surface modification or coating before imaging. (2) suitable for characterizing low-density nanomaterials, offering better contrast. (3) provides 3D images and enables measurement of NPs height. (4) cost much less and occupies smaller laboratory space.¹²⁰⁻¹²² In 2017, S. Al-Anssari et al used AFM to confirm NPs adsorption on calcite surface. They observed that nanofluid-treated calcite exhibited higher surface roughness, also roughness values increasing from 18 to 32 nm on the original calcite surface to 450 to 580 nm when treated at room temperature, and up to 2100 to 2700 nm when treated at higher temperatures (60°C).³⁷

Energy dispersive X-ray spectroscopy (EDS) serves similar purposes as AFM and reveals NPs presence across a nano-treated surface to determine whether they are bound irreversibly or reversibly. It is commonly equipped with electron microscopy to confirm and identify the purity, morphology, mineralogy, and elemental ratio of the synthesized NPS. EDS also has the function of elemental mapping and corresponding colors for specific elements. In 2019, Jagar A. Ali et al used EDS with SEM to present the existence of Si, Zn, and Ca elements within the synthesized nanocomposite.⁴³

The porosity and surface area are important properties required to know for core samples before core flooding tests. N₂ physisorption using the Brunauer, Emmett, and Teller (BET)

equation is the best instrument to be utilized. In 2019, Lady J. Giraldo et al. used the BET equation to calculate the surface area of NiO/SiO₂ Janus NPs. The similarity between the geometrical surface area (calculated from TEM observations) and the calculated surface area (using the BET method) shows that the NPs are likely non-porous.³²

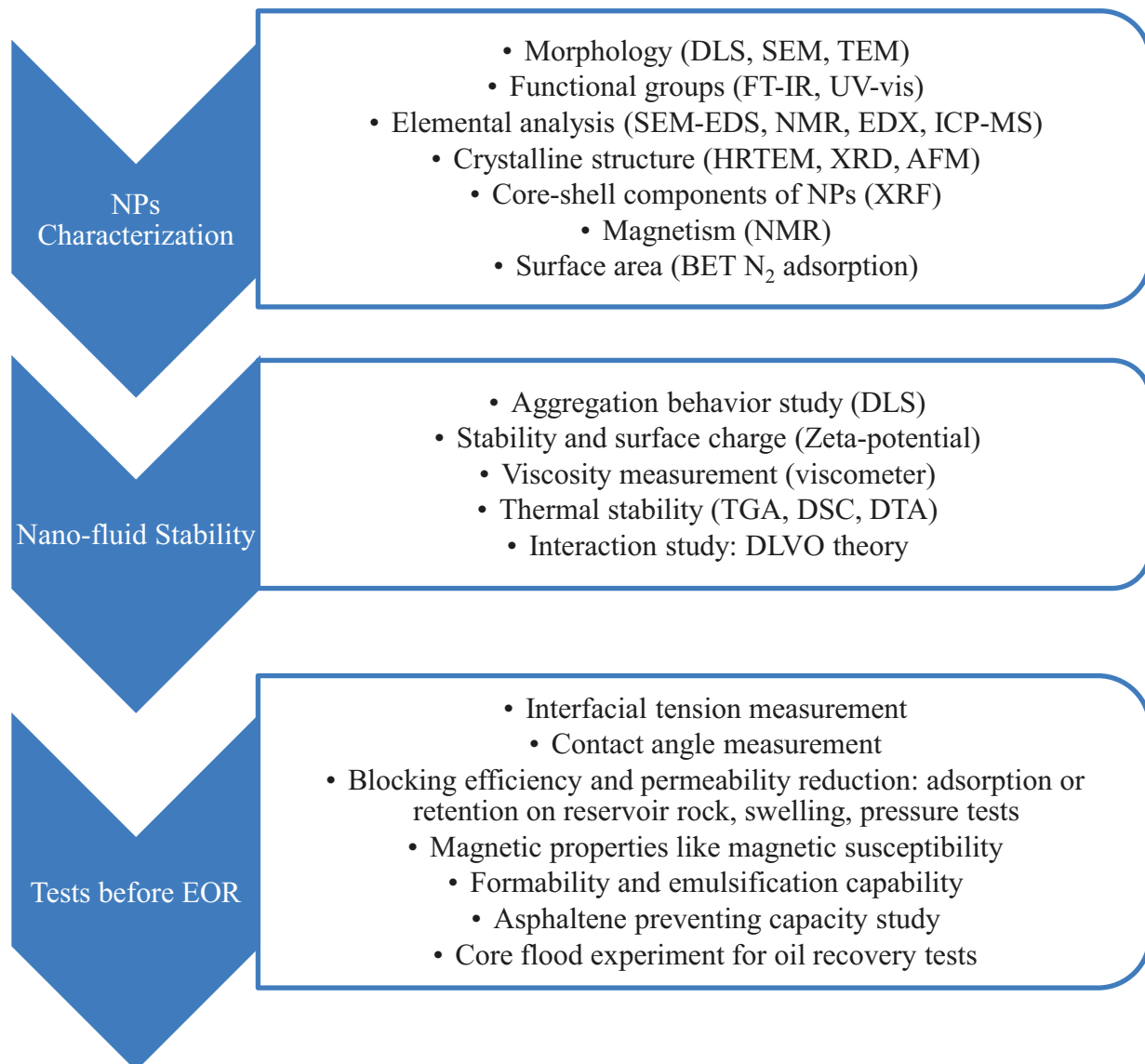


Figure 11. Instruments have been applied to three distinct categories of NanoEOR research work.

6 *Challenges and Opportunities for Future Research*

(1) **Stability under reservoir conditions.** Although SiO₂-based-NPs have proven to increase oil recovery, most of them have only been studied at laboratory bench scales and not at practical field scales. Thus, one of the greatest challenges that remain for further development of these NanoEOR materials and methods is their practical demonstrations in the field. Under high temperatures, salinities, and pressures, NPs tend to aggregate and block the substrate rock pores needed for efficient oil extraction. Surface functionalized SiO₂-based-NPs have shown promise for overcoming the aggregation problem, but more field-scale experimental investigations are still required. The other challenge is that applying the NanoEOR in large-scale production needs to be supported by core flooding experiments. Most research currently focuses on NanoEOR using the glass microbic model or simulations without considering field trials. There are many other influencing factors when applying NanoEOR in field trials therefore without a proper amount of lab work, it can not be cost-effectively applying NanoEOR in field trials.

(2) **Synthesis of SiO₂-based-NPs.** Most of the EOR research performed to date has used purchased SiO₂-based-NPs. However, the opportunity of tuning the properties of SiO₂-based-NPs in terms of size, surface functionality, and charge has been barely explored in terms of optimizing performance and better understanding the NanoEOR mechanisms. The cost of synthesizing SiO₂-based-NPs is a challenge because it's higher than that of other EOR chemicals. This is because production is on a small scale and lacks standardization.

(3) **Mechanisms of NanoEOR.** a thorough understanding of the NanoEOR mechanisms and how NPs interact with reservoir properties and initial reservoir fluid is not enough. Current research is mostly focused on the investigation of IFT and wettability, but the study of

comprehensive mechanisms and potential mechanisms is few. Various reservoir rocks have varying tendencies to adsorb different SiO₂-based-NPs. Specific mechanisms should be considered based on the combination of specific reservoir rocks and NPs. Therefore, studying theoretical aspects and mathematical models for different NanoEOR approaches to grasp the core mechanisms can help engineers in choosing appropriate nano-techniques and minimizing risks during field trial applications.

(5) Health safety and environmental risks. Currently, there is insufficient information about the likelihood or potential hazards of SiO₂-based-NPs remaining underground, penetrating underground aquifers, or otherwise dispersing within the environment. Toxicity is another challenge for the NanoEOR application. While plain SiO₂-NPs are generally non-toxic, research on nanofluid mixtures is still in its early stages. The possible toxicity of the modified SiO₂-based nanofluids should be investigated to improve the safety application of the nanotechnology. Due to NPs' small size, there is a higher potential for inhalation or skin absorption. To reduce these risks, regulatory agencies (e.g., EPA, ISO, and ASTM) should create standards, regulations, recommended practices protocols, and working guidance.

7 *Summary and Conclusions*

Many studies have shown a significant increase in oil recovery when applying SiO₂-based-NPs to EOR. This article reviews the existing studies on using SiO₂-based-NPs in EOR and offers a thorough insight into their applications and related challenges. First, four different preparation methods of SiO₂-based-NPs, two approaches for surface functionalized SiO₂-based-NPs, and SiO₂-based nanofluids have been summarized. Then possible NanoEOR mechanisms include (1) pore channel plugging; (2) decreasing the mobility ratios of the injected fluids; (3) reducing IFT;

(4) altering wettability; and (5) reducing capillary force. Also, the impacts of SiO₂-based-NPs nanofluids on the EOR process have been discussed. Furthermore, this article discusses the utilization of instrumentation in the oil and gas sector, addresses the difficulties related to SiO₂-based-NPs in NanoEOR, and outlines potential directions for future research. Besides the above mentioned, the following conclusions were made: (1) In recent years the non-toxic, economy-efficient, and environmentally friendly NPs like SiO₂-based-NPs and carbon-based nanomaterials showed significant improvement for the NanoEOR applications. This suggests their strong potential for use in field trials. (2) considering the challenges outlined, further research should be aimed at scaling up the production of SiO₂-based-NPs and reducing the cost of producing NPs. (3) when preparing this review we found out that certain types of nanofluids are theoretically better at certain EOR mechanisms, hence, not only SiO₂-based-NPs but also the research on various nanofluid mixtures requires thorough investigations.

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Julia Xiaojun Zhao is a Professor in the Chemistry department at the University of North Dakota. She is working broadly in the field of nanoscience and nanotechnology, with specific training and expertise in the development of silica and carbon-based nanomaterials. As the PI/CoPI Julia has led a total of 6 federal grants including NSF, DoD, and EPA, grants and 17 University- and State- funded grants. Julia has developed several novel silica nanomaterials. These works have resulted in 13 invention disclosures, three of them are issued patents now. Julia has co-authored 76 peer-reviewed publications, 11 book chapters, and one book.

David Pierce is a Professor in the Chemistry department at the University of North Dakota. He has been working for over 30 years in the fields of electrochemistry and ICP-MS, with nanomaterials often used as common substrates for both areas of research.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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ABBREVIATIONS

AFM, atomic force microscopy; ASTM, American Society for Testing and Materials; BET, the Brunauer, Emmett, and Teller; CMC, critical micelle concentration; CTAB, cetyltrimethylammonium; CVD, chemical vapor deposition; DI water, deionized water; DLS, dynamic light scattering; DLVO theory, Derjaguin, Landau, Vervy, and Overbeek theory; DMPA, mercaptobenzimidazole; DSC, differential scanning calorimeter; DTA, differential thermal analysis; DW, distilled water; EDS, energy dispersive X-ray spectroscopy; EOR, enhanced oil recovery; EPA, Environmental Protection Agency; FE-SEM, field emission

scattering electron microscopy; FTIR, Fourier transform infrared spectroscopy; HETEM, high-resolution transmission electron microscopy; ICP-MS, inductively coupled plasma mass spectrometry; IEO, International Energy Outlook; IFT, interfacial tension; ISO, International Standards Organization; LPN, low salinity-polymeric nanofluid; LSWI, low salinity water injection; MPTMOS, 3-(methacryloyloxy) propyl]trimethoxysilane; MWNT, multi-walled nanotube; NC, nanocomposite; NPs, nanoparticles; NMR, nuclear magnetic resonance; OOIP, original oil in place; PVP, polyvinylpyrrolidone; RF, Recovery factor; RMS, root-mean-square; SDS, sodium dodecyl sulfate; SEM, scanning electron microscopy; SiO₂-based-NPs, silica-based nanoparticles; TDS, total dissolved solids; TEM, transmission electron microscopy; TEOS, tetraethylorthosilicate; TGA, thermogravimetric analyser; TTIP, titanium tetra isopropoxide; UV-Vis, ultraviolet-visible; U.S. EIA, the United States Energy Information Administration; VTES, vinyltriethoxysilane; Vo, the volume of oil; Vs, the volume of surfactant; Vw, the volume of water; w/o, water-in-oil; XRD, x-ray diffraction.

REFERENCES

1. Administration, U. S. E. I., US Energy Information Administration, International Energy Outlook with Projection to 2050. US Energy Information Administration Washington, DC, USA: 2021.
2. Abas, N.; Kalair, A.; Khan, N., Review of fossil fuels and future energy technologies. *Futures* **2015**, *69*, 31-49.
3. Zou, C.; Zhao, Q.; Zhang, G.; Xiong, B., Energy revolution: From a fossil energy era to a new energy era. *Natural Gas Industry B* **2016**, *3* (1), 1-11.
4. Ali, A. M.; Yahya, N.; Mijinyawa, A.; Kwaya, M. Y.; Sikiru, S., Molecular simulation and microtextural characterization of quartz dissolution in sodium hydroxide. *Journal of Petroleum Exploration and Production Technology* **2020**, *10* (7), 2669-2684.
5. Surajudeen, S.; Yahya, N.; Soleimani, H.; Musa, A. A.; Afeez, Y.; Rostami, A., EFFECT OF ADSORPTION ON SATURATED SANDSTONE WITHIN ELECTRIC DOUBLE LAYER ON SOLID/LIQUID INTER-PHASE. *Petroleum & Coal* **2019**, *61* (6), 1438-1444.

6. Li, Z.; Kang, W.; Yang, H.; Zhou, B.; Jiang, H.; Liu, D.; Jia, H.; Wang, J., Advances of supramolecular interaction systems for improved oil recovery (IOR). *Advances in Colloid and Interface Science* **2022**, *301*, 102617.
7. Terry, R. E., Enhanced oil recovery. *Encyclopedia of physical science and technology* **2001**, *18* (1), 503-518.
8. Yakasai, F.; Jaafar, M. Z.; Bandyopadhyay, S.; Agi, A., Current developments and future outlook in nanofluid flooding: A comprehensive review of various parameters influencing oil recovery mechanisms. *Journal of Industrial and Engineering Chemistry* **2021**, *93*, 138-162.
9. Sikiru, S.; Yahya, N.; Soleimani, H., Photon–phonon interaction of surface ionic adsorption within electric double layer in reservoir sandstone. *Journal of Materials Research and Technology* **2020**, *9* (5), 10957-10969.
10. Schmidt, D. L., Nanotechnology and Education. In *Women in Nanotechnology: Contributions from the Atomic Level and Up*, Norris, P. M.; Friedersdorf, L. E., Eds. Springer International Publishing: Cham, 2020; pp 29-41.
11. Taniguchi, N., On the basic concept of nanotechnology. *Proceeding of the ICPE* **1974**.
12. Sun, X.; Zhang, Y.; Chen, G.; Gai, Z., Application of Nanoparticles in Enhanced Oil Recovery: A Critical Review of Recent Progress. *Energies* **2017**, *10* (3).
13. Zhou, Y.; Wu, X.; Zhong, X.; Sun, W.; Pu, H.; Zhao, J. X., Surfactant-Augmented Functional Silica Nanoparticle Based Nanofluid for Enhanced Oil Recovery at High Temperature and Salinity. *ACS Applied Materials & Interfaces* **2019**, *11* (49), 45763-45775.
14. Zhou, Y.; Wu, X.; Zhong, X.; Reagen, S.; Zhang, S.; Sun, W.; Pu, H.; Xiaojun Zhao, J., Polymer nanoparticles based nano-fluid for enhanced oil recovery at harsh formation conditions. *Fuel* **2020**, *267*, 117251.
15. Hassani, S. S.; Daraee, M.; Sobat, Z., Advanced development in upstream of petroleum industry using nanotechnology. *Chinese Journal of Chemical Engineering* **2020**, *28* (6), 1483-1491.
16. Hu, Z.; Zhao, J.; Gao, H.; Nourafkan, E.; Wen, D. Transport and Deposition of Carbon Nanoparticles in Saturated Porous Media *Energies* [Online], 2017.
17. Baalousha, M.; Sikder, M.; Prasad, A.; Lead, J.; Merrifield, R.; Chandler, G. T., The concentration-dependent behaviour of nanoparticles. *Environmental Chemistry* **2016**, *13* (1), 1-3.
18. Zallaghi, M.; Kharrat, R.; Hashemi, A., Improving the microscopic sweep efficiency of water flooding using silica nanoparticles. *Journal of Petroleum Exploration and Production Technology* **2018**, *8* (1), 259-269.
19. Al-Anssari, S.; Barifcani, A.; Wang, S.; Maxim, L.; Iglauer, S., Wettability alteration of oil-wet carbonate by silica nanofluid. *Journal of Colloid and Interface Science* **2016**, *461*, 435-442.
20. Hou, B.; Jia, R.; Fu, M.; Wang, Y.; Jiang, C.; Yang, B.; Huang, Y., Wettability alteration of oil-wet carbonate surface induced by self-dispersing silica nanoparticles: Mechanism and monovalent metal ion's effect. *Journal of Molecular Liquids* **2019**, *294*, 111601.
21. Dehghan Monfared, A.; Ghazanfari, M. H., Wettability Alteration of Oil-Wet Carbonate Porous Media Using Silica Nanoparticles: Electrokinetic Characterization. *Industrial & Engineering Chemistry Research* **2019**, *58* (40), 18601-18612.
22. Bila, A.; Stensen, J. Å.; Torsæter, O. Experimental Investigation of Polymer-Coated Silica Nanoparticles for Enhanced Oil Recovery *Nanomaterials* [Online], 2019.
23. Giraldo, J.; Benjumea, P.; Lopera, S.; Cortés, F. B.; Ruiz, M. A., Wettability Alteration of Sandstone Cores by Alumina-Based Nanofluids. *Energy & Fuels* **2013**, *27* (7), 3659-3665.

24. Lim, S.; Horiuchi, H.; Nikolov, A. D.; Wasan, D., Nanofluids Alter the Surface Wettability of Solids. *Langmuir* **2015**, *31* (21), 5827-5835.
25. Ding, H.; Zhang, N.; Zhang, Y.; Wei, M.; Bai, B., Experimental Data Analysis of Nanoparticles for Enhanced Oil Recovery. *Industrial & Engineering Chemistry Research* **2019**, *58* (27), 12438-12450.
26. Rezvani, H.; Riazi, M.; Tabaei, M.; Kazemzadeh, Y.; Sharifi, M., Experimental investigation of interfacial properties in the EOR mechanisms by the novel synthesized Fe₃O₄@Chitosan nanocomposites. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018**, *544*, 15-27.
27. Kazemzadeh, Y.; Sharifi, M.; Riazi, M.; Rezvani, H.; Tabaei, M., Potential effects of metal oxide/SiO₂ nanocomposites in EOR processes at different pressures. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018**, *559*, 372-384.
28. Gholinezhad, S.; Kantzas, A.; Bryant, S. L., Effect of surface functionalized silica nanoparticles on interfacial behavior: Wettability, interfacial tension and emulsification characteristics. *Journal of Molecular Liquids* **2022**, *349*, 118220.
29. Youssif, M. I.; El-Maghraby, R. M.; Saleh, S. M.; Elgibaly, A., Silica nanofluid flooding for enhanced oil recovery in sandstone rocks. *Egyptian Journal of Petroleum* **2018**, *27* (1), 105-110.
30. Yu, J.; Nap, R. J.; Szleifer, I.; Wong, J. Y., Effect of Polymer Surface Modification of Superparamagnetic Iron Oxide Nanoparticle Dispersions in High Salinity Environments. *Langmuir* **2019**, *35* (48), 15864-15871.
31. Al-Anssari, S.; Arif, M.; Wang, S.; Barifcani, A.; Lebedev, M.; Iglauer, S., Wettability of nanofluid-modified oil-wet calcite at reservoir conditions. *Fuel* **2018**, *211*, 405-414.
32. Giraldo, L. J.; Gallego, J.; Villegas, J. P.; Franco, C. A.; Cortés, F. B., Enhanced waterflooding with NiO/SiO₂ 0-D Janus nanoparticles at low concentration. *Journal of Petroleum Science and Engineering* **2019**, *174*, 40-48.
33. Ahmed, A.; Mohd Saaid, I.; M Pilus, R.; Abbas Ahmed, A.; Tunio, A. H.; Baig, M. K., Development of surface treated nanosilica for wettability alteration and interfacial tension reduction. *Journal of Dispersion Science and Technology* **2018**, *39* (10), 1469-1475.
34. Zhao, M.; Lv, W.; Li, Y.; Dai, C.; Wang, X.; Zhou, H.; Zou, C.; Gao, M.; Zhang, Y.; Wu, Y., Study on the synergy between silica nanoparticles and surfactants for enhanced oil recovery during spontaneous imbibition. *Journal of Molecular Liquids* **2018**, *261*, 373-378.
35. Cheraghian, G.; Kiani, S.; Nassar, N. N.; Alexander, S.; Barron, A. R., Silica Nanoparticle Enhancement in the Efficiency of Surfactant Flooding of Heavy Oil in a Glass Micromodel. *Industrial & Engineering Chemistry Research* **2017**, *56* (30), 8528-8534.
36. AfzaliTabar, M.; Alaei, M.; Bazmi, M.; Ranjineh Khojasteh, R.; Koolivand-Salooki, M.; Motiee, F.; Rashidi, A. M., Facile and economical preparation method of nanoporous graphene/silica nanohybrid and evaluation of its Pickering emulsion properties for Chemical Enhanced oil Recovery (C-EOR). *Fuel* **2017**, *206*, 453-466.
37. Al-Anssari, S.; Wang, S.; Barifcani, A.; Lebedev, M.; Iglauer, S., Effect of temperature and SiO₂ nanoparticle size on wettability alteration of oil-wet calcite. *Fuel* **2017**, *206*, 34-42.
38. Rostami, P.; Sharifi, M.; Aminshahidy, B.; Fahimpour, J., Enhanced oil recovery using silica nanoparticles in the presence of salts for wettability alteration. *Journal of Dispersion Science and Technology* **2020**, *41* (3), 402-413.

39. Aghajanzadeh, M. R.; Ahmadi, P.; Sharifi, M.; Riazi, M., Wettability modification of oil-wet carbonate reservoirs using silica-based nanofluid: An experimental approach. *Journal of Petroleum Science and Engineering* **2019**, *178*, 700-710.
40. Mohammadalnejad, P.; Hosseinpour, N.; Rahmati, N.; Rasaei, M. R., Formation damage during oil displacement by aqueous SiO₂ nanofluids in water-wet/oil-wet glass micromodel porous media. *Journal of Petroleum Science and Engineering* **2019**, *182*, 106297.
41. Azarshin, S.; Moghadasi, J.; A Aboosadi, Z., Surface functionalization of silica nanoparticles to improve the performance of water flooding in oil wet reservoirs. *Energy Exploration & Exploitation* **2017**, *35* (6), 685-697.
42. Dai, C.; Wang, X.; Li, Y.; Lv, W.; Zou, C.; Gao, M.; Zhao, M., Spontaneous Imbibition Investigation of Self-Dispersing Silica Nanofluids for Enhanced Oil Recovery in Low-Permeability Cores. *Energy & Fuels* **2017**, *31* (3), 2663-2668.
43. Ali, J. A.; Kolo, K.; Manshad, A. K.; Stephen, K. D., Potential application of low-salinity polymeric-nanofluid in carbonate oil reservoirs: IFT reduction, wettability alteration, rheology and emulsification characteristics. *Journal of Molecular Liquids* **2019**, *284*, 735-747.
44. Kang, H.; Lee, J.; O'Keefe, T.; Tuga, B.; Hogan Jr, C. J.; Haynes, C. L., Effect of (3-aminopropyl)triethoxysilane on dissolution of silica nanoparticles synthesized via reverse micro emulsion. *Nanoscale* **2022**, *14* (25), 9021-9030.
45. Rezaei, S.; Manoucheri, I.; Moradian, R.; Pourabbas, B., One-step chemical vapor deposition and modification of silica nanoparticles at the lowest possible temperature and superhydrophobic surface fabrication. *Chemical Engineering Journal* **2014**, *252*, 11-16.
46. Bachmatiuk, A.; Börrnert, F.; Grobosch, M.; Schäffel, F.; Wolff, U.; Scott, A.; Zaka, M.; Warner, J. H.; Klingeler, R.; Knupfer, M.; Büchner, B.; Rummeli, M. H., Investigating the Graphitization Mechanism of SiO₂ Nanoparticles in Chemical Vapor Deposition. *ACS Nano* **2009**, *3* (12), 4098-4104.
47. Joni, I. M.; Rukiah; Panatarani, C., Synthesis of silica particles by precipitation method of sodium silicate: Effect of temperature, pH and mixing technique. *AIP Conference Proceedings* **2020**, *2219* (1), 080018.
48. Mostajeran Goortani, B.; Mendoza, N.; Proulx, P., Synthesis of SiO₂ Nanoparticles in RF Plasma Reactors: Effect of Feed Rate and Quench Gas Injection. **2006**, *4* (1).
49. Vijayan, V. M.; Tucker, B. S.; Dimble, P. S.; Vohra, Y. K.; Thomas, V., Dusty-Plasma-Assisted Synthesis of Silica Nanoparticles for in Situ Surface Modification of 3D-Printed Polymer Scaffolds. *ACS Applied Nano Materials* **2020**, *3* (8), 7392-7396.
50. Yue, R.; Meng, D.; Ni, Y.; Jia, Y.; Liu, G.; Yang, J.; Liu, H.; Wu, X.; Chen, Y., One-step flame synthesis of hydrophobic silica nanoparticles. *Powder Technology* **2013**, *235*, 909-913.
51. Lee, H. Y.; Cha, C. L.; Hwang, S. S., Combustion synthesis of SiO₂ nanoparticles using flat premixed flame. *International Journal of Hydrogen Energy* **2020**, *45* (45), 24116-24124.
52. Winkler, M. E. G.; da Silva, E. P.; Kunita, M. H.; Rubira, A. F., Synthesis of Silica by Pressured Carbonation and the Influence of CO₂ Pressure on the Silica Properties. *Silicon* **2022**.
53. Zhu, B.; Wei, W.; Ma, G.; Zhuang, Y.; Liu, J.; Song, L.; Hu, X.; Wang, H.; Li, J., A pressurized carbonation sol-gel process for preparing large pore volume silica and its performance as a flattening agent and an adsorbent. *The Journal of Supercritical Fluids* **2015**, *97*, 1-5.
54. Ren, G.; Su, H.; Wang, S., The combined method to synthesis silica nanoparticle by Stöber process. *Journal of Sol-Gel Science and Technology* **2020**, *96* (1), 108-120.

55. Tadanaga, K.; Morita, K.; Mori, K.; Tatsumisago, M., Synthesis of monodispersed silica nanoparticles with high concentration by the Stöber process. *Journal of Sol-Gel Science and Technology* **2013**, 68 (2), 341-345.
56. Meier, M.; Ungerer, J.; Klinge, M.; Nirschl, H., Synthesis of nanometric silica particles via a modified Stöber synthesis route. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018**, 538, 559-564.
57. Keykhosravi, A.; Vanani, M. B.; Daryasafar, A.; Aghayari, C., Comparative study of different enhanced oil recovery scenarios by silica nanoparticles: An approach to time-dependent wettability alteration in carbonates. *Journal of Molecular Liquids* **2021**, 324, 115093.
58. López, D.; Zabala, R. D.; Cárdenas, J. C.; Lopera, S. H.; Riazi, M.; Franco, C. A.; Cortés, F. B., A novel design of silica-based completion nanofluids for heavy oil reservoirs. *Journal of Petroleum Science and Engineering* **2020**, 194, 107483.
59. Rezvani, H.; Panahpoori, D.; Riazi, M.; Parsaei, R.; Tabaei, M.; Cortés, F. B., A novel foam formulation by Al₂O₃/SiO₂ nanoparticles for EOR applications: A mechanistic study. *Journal of Molecular Liquids* **2020**, 304, 112730.
60. Yin, T.; Yang, Z.; Dong, Z.; Lin, M.; Zhang, J., Physicochemical properties and potential applications of silica-based amphiphilic Janus nanosheets for enhanced oil recovery. *Fuel* **2019**, 237, 344-351.
61. Tan, W.; Wang, K.; He, X.; Zhao, X. J.; Drake, T.; Wang, L.; Bagwe, R. P., Bionanotechnology based on silica nanoparticles. *Medicinal Research Reviews* **2004**, 24 (5), 621-638.
62. Jin, Y.; Lohstreter, S.; Pierce, D. T.; Parisien, J.; Wu, M.; Hall, C.; Zhao, J. X., Silica Nanoparticles with Continuously Tunable Sizes: Synthesis and Size Effects on Cellular Contrast Imaging. *Chemistry of Materials* **2008**, 20 (13), 4411-4419.
63. Selvarajan, V.; Obuobi, S.; Ee, P. L. R., Silica Nanoparticles—A Versatile Tool for the Treatment of Bacterial Infections. *Frontiers in Chemistry* **2020**, 8.
64. Chaturvedi, K. R.; Sharma, T., Rheological analysis and EOR potential of surfactant treated single-step silica nanofluid at high temperature and salinity. *Journal of Petroleum Science and Engineering* **2021**, 196, 107704.
65. Jia, H.; Dai, J.; Miao, L.; Wei, X.; Tang, H.; Huang, P.; Jia, H.; He, J.; Lv, K.; Liu, D., Potential application of novel amphiphilic Janus-SiO₂ nanoparticles stabilized O/W/O emulsion for enhanced oil recovery. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2021**, 622, 126658.
66. Liu, R.; Pu, W.; Sheng, J. J.; Du, D., CO₂-switchable nanohybrids for enhancing CO₂ flooding in tight reservoirs: From stable colloids to a relevant viscoelastic fluid. *Materials & Design* **2017**, 133, 487-497.
67. Wu, H.; Gao, K.; Lu, Y.; Meng, Z.; Gou, C.; Li, Z.; Yang, M.; Qu, M.; Liu, T.; Hou, J.; Kang, W., Silica-based amphiphilic Janus nanofluid with improved interfacial properties for enhanced oil recovery. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2020**, 586, 124162.
68. Tajik, S.; Shahrabadi, A.; Rashidi, A.; Jalilian, M.; Yadegari, A., Application of functionalized silica-graphene nanohybrid for the enhanced oil recovery performance. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2018**, 556, 253-265.
69. Zamani, H.; Jafari, A.; Mousavi, S. M.; Darezereshki, E., Biosynthesis of silica nanoparticle using *Saccharomyces cerevisiae* and its application on enhanced oil recovery. *Journal of Petroleum Science and Engineering* **2020**, 190, 107002.

70. Nazarahari, M. J.; Manshad, A. K.; Ali, M.; Ali, J. A.; Shafiei, A.; Sajadi, S. M.; Moradi, S.; Iglauer, S.; Keshavarz, A., Impact of a novel biosynthesized nanocomposite (SiO₂@Montmorilant@Xanthan) on wettability shift and interfacial tension: Applications for enhanced oil recovery. *Fuel* **2021**, 298, 120773.
71. Stöber, W.; Fink, A.; Bohn, E., Controlled growth of monodisperse silica spheres in the micron size range. *Journal of Colloid and Interface Science* **1968**, 26 (1), 62-69.
72. Ibrahim, I. A. M.; Zikry, A. A. F.; Sharaf, M. A., Preparation of spherical silica nanoparticles: Stober silica. *J. Am. Sci* **2010**, 6 (11), 985-989.
73. Guo, Q.; Huang, D.; Kou, X.; Cao, W.; Li, L.; Ge, L.; Li, J., Synthesis of disperse amorphous SiO₂ nanoparticles via sol-gel process. *Ceramics International* **2017**, 43 (1, Part A), 192-196.
74. Fernandes, R. S.; Raimundo, I. M.; Pimentel, M. F., Revising the synthesis of Stöber silica nanoparticles: A multivariate assessment study on the effects of reaction parameters on the particle size. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2019**, 577, 1-7.
75. Wang, X.-D.; Shen, Z.-X.; Sang, T.; Cheng, X.-B.; Li, M.-F.; Chen, L.-Y.; Wang, Z.-S., Preparation of spherical silica particles by Stöber process with high concentration of tetra-ethyl-orthosilicate. *Journal of Colloid and Interface Science* **2010**, 341 (1), 23-29.
76. Kurdyukov, D. A.; Eurov, D. A.; Kirilenko, D. A.; Sokolov, V. V.; Golubev, V. G., Tailoring the size and microporosity of Stöber silica particles. *Microporous and Mesoporous Materials* **2018**, 258, 205-210.
77. Haeri, F.; Rao, D. N., Precise Wettability Characterization of Carbonate Rocks To Evaluate Oil Recovery Using Surfactant-Based Nanofluids. *Energy & Fuels* **2019**, 33 (9), 8289-8301.
78. Zhong, X.; Li, C.; Li, Y.; Pu, H.; Zhou, Y.; Zhao, J. X., Enhanced Oil Recovery in High Salinity and Elevated Temperature Conditions with a Zwitterionic Surfactant and Silica Nanoparticles Acting in Synergy. *Energy & Fuels* **2020**, 34 (3), 2893-2902.
79. Hendraningrat, L.; Li, S.; Torsæter, O., A coreflood investigation of nanofluid enhanced oil recovery. *Journal of Petroleum Science and Engineering* **2013**, 111, 128-138.
80. Roustaei, A.; Bagherzadeh, H., Experimental investigation of SiO₂ nanoparticles on enhanced oil recovery of carbonate reservoirs. *Journal of Petroleum Exploration and Production Technology* **2015**, 5 (1), 27-33.
81. Li, S.; Genys, M.; Wang, K.; Torsæter, O., Experimental Study of Wettability Alteration during Nanofluid Enhanced Oil Recovery Process and Its Effect on Oil Recovery. In *SPE Reservoir Characterisation and Simulation Conference and Exhibition*, 2015; p D031S020R003.
82. Eltoum, H.; Yang, Y.-L.; Hou, J.-R., The effect of nanoparticles on reservoir wettability alteration: a critical review. *Petroleum Science* **2021**, 18 (1), 136-153.
83. Mohsenatabar Firozjahi, A.; Saghafi, H. R., Review on chemical enhanced oil recovery using polymer flooding: Fundamentals, experimental and numerical simulation. *Petroleum* **2020**, 6 (2), 115-122.
84. Rezaei, A.; Abdollahi, H.; Derikvand, Z.; Hemmati-Sarapardeh, A.; Mosavi, A.; Nabipour, N. Insights into the Effects of Pore Size Distribution on the Flowing Behavior of Carbonate Rocks: Linking a Nano-Based Enhanced Oil Recovery Method to Rock Typing *Nanomaterials* [Online], 2020.
85. Rezk, M. Y.; Allam, N. K., Impact of Nanotechnology on Enhanced Oil Recovery: A Mini-Review. *Industrial & Engineering Chemistry Research* **2019**, 58 (36), 16287-16295.

86. Motraghi, F.; Khaksar Manshad, A.; Akbari, M.; Ali, J. A.; Sajadi, S. M.; Iglauer, S.; Keshavarz, A., Interfacial tension reduction of hybrid crude-oil/mutual-solvent systems under the influence of water salinity, temperature and green SiO₂/KCl/Xanthan nanocomposites. *Fuel* **2023**, *340*, 127464.
87. Anovitz, L. M.; Cole, D. R., Characterization and Analysis of Porosity and Pore Structures. *Reviews in Mineralogy and Geochemistry* **2015**, *80* (1), 61-164.
88. Wang, Q.; Yang, S.; Glover, P. W. J.; Lorinczi, P.; Qian, K.; Wang, L., Effect of Pore-Throat Microstructures on Formation Damage during Miscible CO₂ Flooding of Tight Sandstone Reservoirs. *Energy & Fuels* **2020**, *34* (4), 4338-4352.
89. Choi, S. K.; Son, H. A.; Kim, H. T.; Kim, J. W., Nanofluid Enhanced Oil Recovery Using Hydrophobically Associative Zwitterionic Polymer-Coated Silica Nanoparticles. *Energy & Fuels* **2017**, *31* (8), 7777-7782.
90. Ahmadi, R.; Farmani, Z.; Osfouri, S.; Azin, R., Condensate blockage remediation in a gas reservoir through wettability alteration using natural CaCO₃ nanoparticles. *Colloids and Surfaces A: Physicochemical and Engineering Aspects* **2019**, *579*, 123702.
91. Guo, S.; Zheng, H.; Yang, Y.; Zhang, S.; Hou, H.; Zhu, Q.; Du, P., Spatial estimates of surface deformation and topsoil moisture in operating CO₂-EOR project: Pilot environmental monitoring using SAR technique. *Journal of Cleaner Production* **2019**, *236*, 117606.
92. Joshi, D.; Maurya, N. K.; Kumar, N.; Mandal, A., Experimental investigation of silica nanoparticle assisted Surfactant and polymer systems for enhanced oil recovery. *Journal of Petroleum Science and Engineering* **2022**, *216*, 110791.
93. Sorbie, K. S., Polymer-improved oil recovery, 115 glasgow. *Scotland: Blackie & Son* **1991**, 126-163.
94. Gbadamosi, A. O.; Junin, R.; Manan, M. A.; Agi, A.; Yusuff, A. S., An overview of chemical enhanced oil recovery: recent advances and prospects. *International Nano Letters* **2019**, *9* (3), 171-202.
95. Khademolhosseini, R.; Jafari, A.; Shabani, M. H., Micro Scale Investigation of Enhanced Oil Recovery Using Nano/Bio Materials. *Procedia Materials Science* **2015**, *11*, 171-175.
96. de Castro Dantas, T. N.; de Souza, T. T. C.; Dantas Neto, A. A.; Moura, M. C. P. d. A.; de Barros Neto, E. L., Experimental Study of Nanofluids Applied in EOR Processes. *Journal of Surfactants and Detergents* **2017**, *20* (5), 1095-1104.
97. Zhou, Y.; Wu, X.; Zhong, X.; Zhang, S.; Pu, H.; Zhao, J. X., Development of silicon quantum dots based nano-fluid for enhanced oil recovery in tight Bakken cores. *Fuel* **2020**, *277*, 118203.
98. Mohajeri, M.; Hemmati, M.; Shekarabi, A. S., An experimental study on using a nanosurfactant in an EOR process of heavy oil in a fractured micromodel. *Journal of Petroleum Science and Engineering* **2015**, *126*, 162-173.
99. Liu, W.; Luo, L.; Liao, G.; Zuo, L.; Wei, Y.; Jiang, W., Experimental study on the mechanism of enhancing oil recovery by polymer – surfactant binary flooding. *Petroleum Exploration and Development* **2017**, *44* (4), 636-643.
100. Ganiyeva, A.; Karabayanova, L.; Pourafshary, P.; Hashmet, M. R. The Performance of Engineered Water Flooding to Enhance High Viscous Oil Recovery *Applied Sciences* [Online], 2022.
101. Haroun, M.; Rahman, M. M.; Al Kobaisi, M.; Kim, M.; Suboyin, A.; Somra, B.; Abubacker Ponnambathayil, J.; Punjabi, S., Investigation of Hybrid Nanoparticle–Acid Fluids

- (HNAFs): Influence of Wettability and Interfacial Tension Mechanisms in Harsh Carbonate Reservoirs for Improved Oil Recovery. *ACS Omega* **2022**, 7 (45), 40853-40859.
102. Salem Ragab, A. M.; Hannora, A. E., A Comparative Investigation of Nano Particle Effects for Improved Oil Recovery – Experimental Work. In *SPE Kuwait Oil and Gas Show and Conference*, 2015; pp SPE-175395-MS.
 103. Gholamzadeh, Y.; Sharifi, M.; Hemmati-Sarapardeh, A.; Rafiei, Y., Toward mechanistic understanding of interfacial tension behavior in nanofluid-model oil systems at different asphaltene stability conditions: The roles of nanoparticles, solvent, and salt concentration. *Geoenergy Science and Engineering* **2023**, 222, 211449.
 104. Zhang, Z.; Azad, M. S.; Trivedi, J. J., IFT or wettability alteration: What is more important for oil recovery in oil-wet formation? *Fuel* **2021**, 291, 119986.
 105. Nwidee, L. N.; Lebedev, M.; Barifcani, A.; Sarmadivaleh, M.; Iglauer, S., Wettability alteration of oil-wet limestone using surfactant-nanoparticle formulation. *Journal of Colloid and Interface Science* **2017**, 504, 334-345.
 106. Teklu*, T. W.; Alameri, W.; Kazemi, H.; Graves, R. M., Contact Angle Measurements on Conventional and Unconventional Reservoir Cores. In *Unconventional Resources Technology Conference, San Antonio, Texas, 20-22 July 2015*, Society of Exploration Geophysicists, American Association of Petroleum Geologists, Society of Petroleum Engineers: 2015; pp 2297-2311.
 107. Ali, J. A.; Kalthury, A. M.; Sabir, A. N.; Ahmed, R. N.; Ali, N. H.; Abdullah, A. D., A state-of-the-art review of the application of nanotechnology in the oil and gas industry with a focus on drilling engineering. *Journal of Petroleum Science and Engineering* **2020**, 191, 107118.
 108. McElfresh, P.; Holcomb, D.; Ector, D., Application of Nanofluid Technology to Improve Recovery in Oil and Gas Wells. In *SPE International Oilfield Nanotechnology Conference and Exhibition*, 2012; pp SPE-154827-MS.
 109. Chengara, A.; Nikolov, A. D.; Wasan, D. T.; Trokhymchuk, A.; Henderson, D., Spreading of nanofluids driven by the structural disjoining pressure gradient. *Journal of Colloid and Interface Science* **2004**, 280 (1), 192-201.
 110. Wasan, D.; Nikolov, A.; Kondiparty, K., The wetting and spreading of nanofluids on solids: Role of the structural disjoining pressure. *Current Opinion in Colloid & Interface Science* **2011**, 16 (4), 344-349.
 111. Wasan, D. T.; Nikolov, A. D., Spreading of nanofluids on solids. *Nature* **2003**, 423 (6936), 156-159.
 112. Peng, H.; Zhang, Z.; Wang, Z., Dispersion of TiO₂ Nanoparticles in TiO₂/HIPS Composites. *Journal of Dispersion Science and Technology* **2005**, 26 (2), 203-206.
 113. Zhang, H.; Ramakrishnan, T. S.; Nikolov, A.; Wasan, D., Enhanced Oil Recovery Driven by Nanofilm Structural Disjoining Pressure: Flooding Experiments and Microvisualization. *Energy & Fuels* **2016**, 30 (4), 2771-2779.
 114. Esfandyari Bayat, A.; Junin, R.; Samsuri, A.; Piroozian, A.; Hokmabadi, M., Impact of Metal Oxide Nanoparticles on Enhanced Oil Recovery from Limestone Media at Several Temperatures. *Energy & Fuels* **2014**, 28 (10), 6255-6266.
 115. Khoramian, R.; Kharrat, R.; Golshokoo, S., The development of novel nanofluid for enhanced oil recovery application. *Fuel* **2022**, 311, 122558.
 116. Zhang, B.; Mohamed, A. I. A.; Goual, L.; Piri, M., Pore-scale experimental investigation of oil recovery enhancement in oil-wet carbonates using carbonaceous nanofluids. *Scientific Reports* **2020**, 10 (1), 17539.

117. You, Q.; Wang, H.; Zhang, Y.; Liu, Y.; Fang, J.; Dai, C., Experimental study on spontaneous imbibition of recycled fracturing flow-back fluid to enhance oil recovery in low permeability sandstone reservoirs. *Journal of Petroleum Science and Engineering* **2018**, *166*, 375-380.
118. Măntele, W.; Deniz, E., UV–VIS absorption spectroscopy: Lambert-Beer reloaded. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* **2017**, *173*, 965-968.
119. Pellegrino, F.; Pellutiè, L.; Sordello, F.; Minero, C.; Ortel, E.; Hodoroaba, V.-D.; Maurino, V., Influence of agglomeration and aggregation on the photocatalytic activity of TiO₂ nanoparticles. *Applied Catalysis B: Environmental* **2017**, *216*, 80-87.
120. Qiu, H.; Gao, Y.; Boott, C. E.; Gould, O. E. C.; Harniman, R. L.; Miles, M. J.; Webb, S. E. D.; Winnik, M. A.; Manners, I., Uniform patchy and hollow rectangular platelet micelles from crystallizable polymer blends. *Science* **2016**, *352* (6286), 697-701.
121. Pitto-Barry, A.; Perdigao, L. M. A.; Walker, M.; Lawrence, J.; Costantini, G.; Sadler, P. J.; Barry, N. P. E., Synthesis and controlled growth of osmium nanoparticles by electron irradiation. *Dalton Transactions* **2015**, *44* (47), 20308-20311.
122. Hubenthal, F.; Blázquez Sánchez, D.; Träger, F. Determination of Morphological Parameters of Supported Gold Nanoparticles: Comparison of AFM Combined with Optical Spectroscopy and Theoretical Modeling versus TEM *Applied Sciences* [Online], 2012, p. 566-583.

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