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Enhancing Oil Recovery with Shape-Modified Silica Nanoparticles: Efficiency in Oil-Wet Sandstone Reservoirs via Imbibition and Micromodel Approaches

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functionalized with sodium (C14–16) olefin sulfonate (SOS) for enhancing oil recovery in oil-wet sandstone reservoirs. Characterization techniques, including scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET), Thermogravimetric analysis (TGA), and Fourier transform infrared spectroscopy (FTIR), verified successful surface modification. Functionalization reduced the mean particle size from 188 ± 15 to 98 ± 14 nm and enhanced stability, with zeta potential increasing from -11 to -46 mV. Nanoemulsion tests showed that SOS-functionalized nanoparticles achieved the lowest creaming degree and produced smaller oil droplets. The interfacial tension

the lowest creaming degree and produced smaller oil droplets. The interfacial tension between crude oil and SOS-functionalized nanoparticles decreased from 24 to 1 mN/m, with further reductions observed upon the addition of alkali. Wettability alteration was also achieved, with contact angles shifting from 20° (oil-wet) to 173° (strongly waterwet) in the presence of SOS-functionalized nanoparticles. Spontaneous imbibition tests demonstrated oil recoveries of 77% with SOS-functionalized nanoparticles, outperforming SOS alone (42%) and unmodified nanoparticles (35%). Micro-CT scanning of the samples after imbibition test showed lower pore connectivity reduction with SOS-functionalized nanoparticles (31%) compared to unmodified nanoparticles (59%). Micromodel flooding tests confirmed enhanced oil recovery, with SOS-functionalized nanoparticles achieving 86% recovery compared to SOS (38%) and unmodified nanoparticles (18%). This study highlights the potential of SOS-functionalized silica nanoparticles to improve oil recovery in oil-wet sandstone reservoirs through wettability alteration, interfacial tension reduction, and stabilized emulsions.

1. INTRODUCTION

The global energy demand is expected to rise by approximately 50% in the next two decades. With easily accessible oil depleting, the energy supply will increasingly depend on unconventional sources and enhanced oil recovery (EOR) processes.^{1–3} EOR involves methods beyond traditional reservoir energy management and pressure maintenance techniques, such as gas and water injection.^{3,4} Various EOR strategies, including thermal, chemical, and gas-based methods, have been developed to improve oil recovery.^{5,6} Despite their potential, these traditional approaches often exhibit limitations such as low recovery efficiency, high operational costs, and the risk of reservoir damage.^{7,8}

In recent years, nanotechnology-based EOR techniques have shown significant potential in addressing the challenges of traditional methods. Over the past decade, studies have investigated the application of nanomaterials, such as nanoparticles (NPs), nanocomposites, nanofluids, and quantum dots, in various oil reservoirs.^{9–14} These materials enhance the performance of conventional EOR agents, including surfactants, polymers, and foams.^{6,15–17} Their unique properties, such as small size, high surface-to-volume ratio, cost-effectiveness, and environmentally friendly characteristics, contribute to this enhancement. $^{8,16}\!\!$

(%)

EOR

Nanotechnology optimizes EOR processes in several ways. It enables precise surfactant delivery to improve wettability alteration at the oil–water interface. It also enhances fluid mobility, solubility, stability, and distribution within the reservoirs. Furthermore, nanomaterials offer customizable properties, including shape, size, porosity, and functionality. Their application supports sustainable practices and improves cost efficiency, making EOR operations economically viable.^{8,18,19}

Extensive research has been conducted to optimize the use of NPs in EOR by evaluating the chemical and physical factors influencing their effectiveness. Key factors include ionic composition, particle size, and concentration.^{8,19} Early studies

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focused on nanosolid particles such as silica (SiO_2) , aluminum oxide (Al₂O₃), titanium dioxide (TiO₂), zirconium dioxide (ZrO_2) , iron (II, III) oxide (Fe₃O₄), and zinc oxide (ZnO).^{20–23} Among these, SiO₂ NPs have demonstrated significant potential for EOR due to their nontoxic nature and their ability to enhance oil recovery by modifying surface properties.^{8,11,16,18,24} Their small size allows them to penetrate micro- and nanoscale pores in sandstone substrates, which are inaccessible to larger injection fluids like polymers.²⁵⁻²⁹ This enables SiO₂ NPs to displace trapped oil more effectively.²⁹ Additionally, SiO₂ NPs possess a higher surface-to-volume ratio, enhancing their reactivity and interaction with surfaces.^{8,30,31} Sikiru et al. investigated the behavior of surface ions and charges within the electric double layer in reservoir sandstone. Their findings revealed that negatively charged SiO₂ NPs increased repulsion between oil and mineral surfaces, leading to enhanced oil mobility.^{5,32} Youssif et al. demonstrated the effectiveness of hydrophilic SiO₂ NPs in tertiary oil recovery, achieving a 13.28% increase in recovery compared to water flooding in sandstone reservoirs.³³

Surface modification of SiO₂ NPs is critical for tailoring their properties to specific reservoir conditions.^{34–37} NP-assisted surfactants exhibit superior stability and adaptability in oil reservoirs compared to surfactants alone.^{37–40} These NPs act as nanocarriers and protective agents preventing surfactant precipitation, adsorption, and degradation under harsh conditions.^{18,41–45} They also enhance interfacial tension (IFT) reduction by increasing adsorption at the oil–water interface, resulting in improved EOR efficiency.^{18,46} Zargartalebi et al. reported that SiO₂ NPs in surfactant solutions reduced surfactant adsorption and improved IFT behavior in surfactant–oil systems.⁴⁷ Comparative studies further confirmed that SiO₂ NPs are effective in reducing the IFT, making them ideal for forming NP-surfactant assemblies in EOR.^{34,38}

In another study, Ihekoronye et al. studied the effects of biosurfactants derived from yellow oleander seed oil combined with different NPs on EOR in Niger Delta oil fields.⁴⁸ Core flooding tests demonstrated that the NP-surfactants combination altered wettability and reduced IFT, significantly enhancing oil recovery compared to conventional methods.⁴⁸ Rezaei et al. investigated the combination of α -olefin sulfonate (AOS) surfactant with hydrophilic SiO₂ NPs for EOR in carbonate reservoirs.⁴⁹ AOS reduced the oil–water IFT, with further reductions observed when SiO₂ NPs were incorporated. Core flooding experiments showed that the AOS-SiO₂ NP solution increased oil recovery by 3% in carbonate cores with homogeneous pore size distribution and 9% in those with heterogeneous pore sizes.⁴⁹

Several studies have also examined the primary modification of SiO₂ NPs with different chemicals before combining them with surfactants. Zhao et al. used premodified SiO₂ NPs treated with the lauramidopropyl hydroxy sulfobetaine surfactant.⁵⁰ The resulting nanofluid demonstrated strong stability, interfacial activity, and wettability alteration properties. Spontaneous imbibition tests showed a 35% oil recovery with the SiO₂ nanofluid, compared to 5.53% with formation water.⁵⁰ Liu et al. utilized premodified SiO₂ NPs (amine-terminated NPs) combined with a nonionic surfactant (laurel anolamide) through hydrogen bonding interactions. Micromodel flooding experiments demonstrated a cumulative oil recovery of 70.9%, with an additional 29.2% recovery under heterogeneous conditions.⁵ Similarly, Zhou et al. synthesized amino-modified SiO₂ NPs via a reverse microemulsion method using TEOS and APTES to graft amino groups onto the SiO₂ surface.¹⁸ These modified NPs were

combined with the anionic surfactant (soloterra 964) to form a nanofluid. Spontaneous imbibition tests showed an oil recovery of 47%, outperforming individual components such as brine (11%), surfactant alone (23%), or amino-modified SiO₂ NPs (17%). This enhancement was attributed to reduced IFT, wettability alteration, and the synergistic interaction between NPs and surfactants.¹⁸

Kumar et al. formulated a nanofluid using positively charged Ludox CL SiO₂ NPs with the aerosol-OT (AOT) surfactant, achieving synergistic effects.⁵² This nanofluid reduced IFT, altered sandstone wettability from oil-wet to water-wet, and demonstrated superior oil recovery during spontaneous imbibition test.⁵²

Previous studies have highlighted the advantages of combining SiO_2 NPs with surfactants for EOR, such as improved wettability and IFT reduction. However, these approaches often rely on physical mixing without prior functionalization, leading to NP aggregation under reservoir conditions. This aggregation may block reservoir pores and reduce the permeability, ultimately diminishing the EOR efficiency. Furthermore, the existing synthesis process often involves primary grafting of NPs before surfactant functionalization, requiring multiple and energy-intensive steps. These limitations highlight the need for cost-effective and efficient grafting methods to enhance EOR performance.

Furthermore, the functionalization of NPs with surfactants has been reported to improve EOR by facilitating the spontaneous formation of oil-in-water emulsions without external energy.^{53–58} This mechanism, increasingly recognized as crucial for EOR, facilitates the expansion of connate water in the reservoir, thereby enhancing the release of trapped oil.^{57,59}

In addition to chemical properties, the shape and structure of NPs significantly influence their effectiveness in EOR applications.^{8,60} Understanding the petrophysical properties of reservoir rocks, such as sandstones, is vital for designing and optimizing NPs and nanofluids.^{61–63} These properties are critical for minimizing operational risks and enhancing hydrocarbon recovery.^{61,64} Key petrophysical properties, such as porosity and permeability, are fundamentally determined by the geometric characteristics of the pore spaces in these rocks.⁶⁴

Historically, most EOR studies have focused on spherical NPs, such as SiO₂, which are effective for oil displacement.^{60,65,66} However, the potential advantages of nonspherical particle morphologies remain underexplored.⁶⁰ Recent studies suggest that the synthetic parameters of SiO₂ NPs, including their morphology, significantly impact their performance.^{67,68} Nonspherical particles could offer enhanced benefits in oil recovery processes by better matching the pore geometries of specific reservoirs.^{67,68}

Researchers are working to control the structural parameters of mesoporous SiO₂ NPs to address diverse reservoir conditions.⁶⁹ Surfactant-assisted self-assembly is a promising method for synthesizing mesoporous SiO₂ materials with tailored morphologies and structures.^{69,70} Single surfactants such as polyvinylpyrrolidone and cetyltrimethylammonium bromide (CTAB), are commonly used to control the dimensions of SiO₂ nanorods.^{70–72} Han et al.⁶⁹ synthesized mesoporous SiO₂ NPs in different shapes, including spherical, shell-like, rugby ball-like, peanut-shaped, hollow, and yolk–shell structures. They achieved this by adjusting the concentration of dodecanol (C₁₂–OH) and the reaction temperature. Similarly, Khademolhosseini et al.⁶⁰ synthesized spheroid-like SiO₂ NPs by titrating potassium silicate with hydrochloric acid. Their



Figure 1. Workflow illustrating the process of converting pore structures extracted from thin-section images to facilitate the detection and quantification of pores within rock samples.

results showed that particle size decreased with higher temperatures and increased the potassium silicate concentration. However, their method required additional modification steps to fine-tune SiO_2 NPs morphology.

Despite these advancements, synthesizing mesoporous SiO_2 structures with capsulated shapes remains a challenge. Current methods often involve multiple steps or specialized conditions, limiting their scalability and applicability. To the best of our knowledge, no existing studies have reported the synthesis of mesoporous SiO_2 NPs with a capsulated shape using a one-step approach. Developing a straightforward, scalable method for producing SiO_2 NPs with a sustainable morphology is crucial for advancing EOR processes. Such a method should integrate readily available surfactants while accounting for the pore structures and sizes of reservoir rocks.

This study introduces a novel approach for synthesizing and characterizing capsulated SiO_2 NPs tailored for EOR applications in oil-wet sandstone reservoirs. Unlike conventional methods, the NPs were directly functionalized with the sodium (C14–16) olefin sulfonate (SOS) surfactant. This approach eliminates the need for energy-intensive primary grafting steps. The synthesis process was optimized to match the pore dimensions and connectivity of Berea sandstone reservoirs, characterized using X-ray microcomputed tomography (X-ray Micro-CT).

Advanced characterization techniques were employed to evaluate the functionalized NPs. These included scanning electron microscopy (SEM)-energy dispersive X-ray spectroscopy (EDX), Brunauer–Emmett–Teller (BET), thermogravimetric analysis (TGA), Fourier transform infrared spectroscopy (FTIR), zeta potential (ZP) analysis, dynamic light scattering (DLS), IFT measurements, and contact angle measurements. Oil/water emulsions were prepared in both the absence and presence of alkali to identify the optimal alkali concentration. Surfactant-functionalized SiO₂ NPs were then utilized to enhance the stability of these emulsions. Emulsion stability was examined through creaming degree measurements, droplet size distribution analysis using a MasterSizer instrument, and microscopic imaging.

Additionally, imbibition testing combined with X-ray Micro-CT investigations was performed to investigate the potential of SOS-functionalized SiO_2 for enhancing oil displacement efficiency. The movement and interactions of these NPs within a physically modeled sandstone microchip were analyzed using custom-developed software. This software integrated advanced statistical modeling with automated image processing workflows, incorporating tools such as OpenCV framework, dynamic thresholding, and Gaussian blurring. These techniques provide a foundation for understanding the behavior of functionalized NPs and their applicability to EOR in oil-wet sandstone reservoirs.

2. EXPERIMENTAL METHODS

2.1. Materials and Chemicals. In this study, the synthesis of capsule-shaped SiO2 NPs was carried out using tetraethyl orthosilicate (TEOS), dodecanol, cetyltrimethylammonium bromide (CTAB), and sodium hydroxide (NaOH), all of which were purchased from Sigma-Aldrich, and used without further modification. Additional reagents, including potassium chloride, magnesium chloride, sodium chloride, sodium carbonate, calcium chloride, and sodium hydroxide were sourced from VWR and also utilized as received. For the surface modification of SiO₂ NPs to generate nanofluids, sodium (C14-16) olefin sulfonate (SOS) surfactant, supplied by Stepan UK, Ltd., was employed. The dispersion medium for nanoparticle preparation was deionized water (DW) with a resistivity of 18.2 M\Omega $\cdot cm$ and a total organic carbon (TOC) content of ≤ 5 . To accurately simulate oil reservoir conditions, the study used Algerian dead crude oil, industrially evaluated by a viscosity of 71 cP at 20 °C, decreasing to 13 cP at 60 °C, and an API gravity of 24.6. The asphaltene content was approximately 0.25%. Additionally, sandstone core samples with a porosity range of 20 to 22% were employed to closely replicate the reservoir environment.

2.2. Evaluation of Sandstone Reservoir Rocks: Pore Size and Connectivity for Presynthesis Process of Shaped SiO₂ NPs. In the industrial application of EOR, quantifying pore connectivity presents one of the most critical and complex tasks for accurately modeling the transport properties of reservoir rocks. This process is essential for determining the pore throat size, which plays a pivotal role



Figure 2. Schematic representation of the synthesis process for capsule-shaped SiO₂–S NPs.

in defining the permeability of porous rocks. Permeability is crucial for designing the optimal shape and size of NPs in the nanofluids that will be injected into the reservoir's pore spaces. CT imaging technology is found to offer a valuable tool for constructing three-dimensional digital models of reservoir cores, enabling the imaging and digitization of both pore space and the formation matrix in natural rock samples. Besides, this technique facilitates the precise and rapid quantification of pore type, size, and connectivity, offering significant advantages in characterizing rock pore structures without damaging the sample.^{73,74}

Through CT scanning, this study bridges the gap between the microstructure and the macroscopic physical properties of core samples, complementing experimental limitations and providing a comprehensive multiscale analysis of Berea sandstone cores, as prerequisite for the effective shape and size of injected SiO_2 NPs.

Four sandstone core samples (two fresh and two saturated with nanofluids) were sectioned into smaller pieces $(2 \text{ cm} \times 3 \text{ cm})$ from dry and imbibition-tested cores. The samples were then polished and aircleaned for thin-section image acquisition and mounted on aluminum



Figure 3. Schematic representation of the functionalization process of SiO₂-S NPs with the SOS surfactant.

rods with a diameter of 1.6 mm and length of 2.5 cm. Fresh-dried sandstone samples were initially analyzed to determine the pore size, suitable for accommodating synthesized control SiO₂ and surfactant-functionalized SiO₂ NPs. For further comparison, the saturated samples were also analyzed after imbibition tests to assess the performance of the control and surfactant-functionalized SiO₂ NPs.

X-ray micro-CT scanning was conducted on the core plugs by using a Zeiss Xradia Versa 410 Micro-CT at the University of Leeds. Initial scans were performed on a 19.4×25 mm field at a resolution of $10 \,\mu$ m, followed by a finer scan on a 5.9×6.4 mm field with a resolution of 4 μ m. The scanning voltage and current were set to 60 kV and 15 μ A, respectively, ensuring sufficient X-ray penetration. The CT scan

produced 1601 two-dimensional (2D) tomographic images (with a pixel size of 6.3 and an exposure time of 5 s), which were reconstructed into three-dimensional (3D) scale images using a back-projection algorithm. The Avizo 2020.1 graphic software was used for scale segmentation of the reconstructed images, extracting the pore system from the rock matrix based on variations in X-ray attenuation across materials of different densities.

The analysis workflow comprised four key steps:

- (i) Imaging the sandstone core samples (both fresh and saturated) for pore network modeling.
- (ii) Extracting the pore network from images using a color threshold-based method.
- (iii) Developing a connected component labeling algorithm to label pores based on pixel connectivity, followed by implementing an enhanced watershed algorithm to detect pore bodies and throats within the complex pore system, for calculating the incremental pore areas and corresponding throat sizes (see Figure 1).
- (iv) Utilizing a maximum spherical algorithm for pore network modeling to differentiate between pore and throat bodies by probing spheres with varying radii within the pore system. The largest spheres were designated as pores, while the smaller ones in between were identified as throats. The pore and throat configurations were visualized in 3D, where pores were represented by superimposed spheres of various diameters, and throats were depicted as cylinders connecting the spheres, each with different lengths and diameters. The numbers, volumes, radii of pores, connectivity, and coordination numbers were quantified through pore network modeling.

2.3. Synthesis and Characterization of Nanoparticles. 2.3.1. Synthesis of Capsule-Shaped NPs. Capsule-shaped SiO_2 NPs were synthesized using a one-step sol-gel method, with two samples prepared to identify the optimal conditions by varying the dodecanol concentration. Initially, 20 mg of dodecanol was dispersed in 20 mL of DW (forming a concentration of 1 mg/mL). This solution, designated as Solution 1, was stirred at 800 rpm and 60 °C for 30 min to achieve complete dispersion. Separately, 30 mg of NaOH was dissolved in 30 mL of DW, followed by the addition of 100 mg of CTAB. The mixture was gently stirred at 200 rpm and 60 °C for 30 min, producing Solution 2.

Solution 1 was then gradually added to Solution 2 dropwise over a period of 5 min, and the combined mixture was stirred at 350 rpm and 60 °C for an additional 30 min. Subsequently, 0.8 mL of TEOS was introduced into the mixture dropwise over 20 min using a Harvard PHD 4400 syringe pump. The reaction was maintained under continuous stirring at 350 rpm and 60 °C for 2 h to ensure a complete formation of the SiO₂ NPs. After the reaction, the resulting mixture was centrifuged at 10,000 rpm for 15 min to separate the NPs. The resultant precipitate was washed twice with DW and four times with ethanol to remove any remaining CTAB. To preserve the structural integrity of the NPs, the washed precipitate was rapidly frozen in a liquid nitrogen bath (-196°) for 10 min and subsequently subjected to freeze-drying for 48 h. The final product was labeled as SiO₂–S20 NPs.

To evaluate the effect of increased dodecanol content on the morphology of the NPs, the same synthesis protocol was repeated with the dodecanol concentration increased to 1.5 mg/mL, archived by dispersing 30 mg of dodecanol in 20 mL of DW. The sample was labeled as SiO₂–S NPs. This comparative approach facilitated the selection of optimally structured capsule-shaped SiO₂ NPs suitable for EOR applications. A schematic representation of the synthesis process for SiO₂–S NPs is provided in Figure 2.

2.3.2. Functionalization of SiO_2 -S NPs with the SOS Surfactant. In this study, the synthesized SiO_2 -S NPs were functionalized with SOS surfactant to assess their stability and potential applicability in the EOR process. The functionalization was conducted directly on the NPs without the need for primary modification, aiming to enhance their surface properties for EOR applications. The functionalization process started with the determination of the optimal SiO₂-S NPs to SOS ratio. Specifically, 100 mg of SiO₂-S NPs were modified using varying concentrations of the SOS surfactant. The detailed procedure for

selecting the optimal SiO₂-S NPs to SOS ratio is provided in Section SI2 of the Supporting Information (SI). Based on these findings, a ratio of 1:1.5 was identified as the most effective for functionalization. Experimentally, 100 mg of SiO₂-S NPs was dispersed in 50 mL of DW, followed by stirring at 300 rpm for 30 min at 60 °C to ensure complete dispersion (referred to as Solution 1). Separately, 150 mg of SOS was dissolved in 25 mL of DW and gently stirred at 100 rpm for 30 min at 60 °C to achieve a homogeneous solution (referred to as solution 2). Solution 1 was then gradually added to solution 2 dropwise over 8 min to ensure the effective interaction between the SOS and the surface of SiO₂-S NPs. To ensure an in-depth interaction and stable attachment of SOS molecules, the resultant mixture was continuously stirred at 120 rpm and 60 °C for 24 h. Following this, the mixture was centrifuged at 5000 rpm for 15 min, after which the supernatant was carefully decanted to isolate the functionalized NPs. The precipitate was washed three times with DW to eliminate any unbound SOS molecules. Finally, the washed NPs were frozen for 10 min in a liquid nitrogen bath at -196 °C and freeze-dried for 48 h to sublimate the frozen water. The final product was labeled as SOS-S NPs. The step-by-step functionalization process of SiO2-S NPs with SOS surfactant is illustrated in Figure 3.

2.3.3. Nanoparticle Characterization. 2.3.3.1. Scanning Electron Microscope (SEM) and Brunauer-Emmet-Teller (BET) Analyses. In this study, the morphology, size, and structural characteristics of the synthesized nanomaterials, both before and after surface modification, were examined using a cold field emission scanning electron microscope (Hitachi SU8230 CFE-SEM). This advanced imaging technique allowed for high-resolution visualization of the nanoparticle surfaces, providing detailed insights into their physical properties. Energy dispersive X-ray spectroscopy (EDX) from OXFORD instruments was employed in combination with SEM to analyze surface chemical compositions of nanomaterials. A small quantity of each sample (~0.6 mg) was dispersed in 5 mL of DW and subjected to bath sonication for approximately 5 min to ensure the suspension of the NPs and enable accurate imaging. The SEM imaging was performed using an acceleration voltage of 2 kV, which was selected to optimize the resolution and contrast of the NPs' images. To evaluate the influence of SOS loading on the surface characteristics of SiO₂-S NPs, the Brunauer-Emmet-Teller (BET)-gas adsorption-desorption method was employed using a Micromeritics Tristar 3000 system. This method is essential for analyzing the surface area and pore size of porous materials, particularly in micro- and mesoporous structures. Samples in their solid form were initially degassed using a Micromeritics Flow Prep 060 degassing System. This process involved heating the samples to 150 °C overnight under a flow of nitrogen gas to remove any moisture and impurities from their surfaces and pores. After being degassed, the samples were weighed to ensure precise software calculations. These samples were then subjected to nitrogen adsorption-desorption at (-196 °C) to produce adsorption-desorption isotherms.

2.3.3.2. Thermogravimetric (TGA) and Fourier Transform Infrared Spectroscopy (FTIR) Analyses. TGA and FTIR analyses were employed to perform a comprehensive qualitative analysis of the functional groups present in the samples. In this study, a Nicolet iS10 from ThermoFisher Scientific was utilized to identify the principal functional groups and molecular bonds in SiO₂-S NPs, both before and after the functionalization with the SOS agent. Samples were prepared by mixing 6 mg of each sample with 500 mg of KBr and then placing them on a DRIFTS holder. The analyses were conducted in transmission mode, covering a spectral range from 400 to 4000 cm⁻¹ with a resolution of 2 cm^{-1} . Each spectrum was averaged over 128 scans. The quantity of SOS grafted onto the surface of SiO₂-S NPs was determined using TGA analysis (TGA – Mettler Toledo TGA/DSC1). The samples were analyzed in their solid state without any purification process. Approximately 10 mg of each sample was placed in a 70 μ L alumina crucible and positioned in the TGA/DSC1 sample holder. TGA measurements were carried out systematically over a temperature range from 30 to 900 °C, with a heating rate of 10 °C/min, under a steady airflow of 50 mL/min.

2.3.4. Characterization of Nanofluids. 2.3.4.1. Zetasizer and Dynamic Light Scattering (DLS). The stability and surface charge of

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core samples	length (cm)	diameter (cm)	dry weight (g)	pore volume (cm ³)	porosity (%)	permeability (mD)
S1	4.058	3.828	95.185	10.145	21.720 ± 0.004	443.250 ± 13.430
S2	4.030	3.827	94.765	10.027	21.638 ± 0.005	450.250 ± 13.640
S3	4.157	3.831	97.237	10.855	22.648 ± 0.004	449.030 ± 13.610

the nanofluids were evaluated at room temperature by using a Malvern Zetasizer Nano ZS/ZSP (MRK654-01) instrument. The analyses were performed in automatic mode, employing the Smoluchowaski approximation for aqueous systems. An equilibration time of 60 s at ambient temperature was set.

In our previous research,⁷⁵ the effect of salinity on NPs stability and EOR performance was thoroughly studied. Low salinity water (LSW) with 500 ppm of NaCl was identified as optimal, providing a balance between stability and performance. This salinity level was therefore selected as the dispersant solvent for the NPs in this study. A nanofluid concentration of 100 ppm was used, based on preliminary screening of IFT measurements and nanoemulsions, as detailed in Section 2.3.5.

To investigate the impact of alkali on nanofluid stability, ZP and DLS measurements were conducted without and with 0.1 wt % alkali. The samples were designated as N1 (without alkali) and N2 (with alkali). A small volume of each sample was injected into 1 mL of disposable cells using a syringe. Three measurements were collected per sample, and the arithmetic average was recorded. To ensure accuracy, each measurement was repeated three times. Additionally, particle size distributions of the nanofluids were also determined by using DLS with the same instrument.

2.3.4.2. Interfacial Tension (IFT) Measurements. IFT experiments were conducted to evaluate the ability of modified SiO_2-S NPs with SOS surfactant to reduce IFT compared to unmodified SiO_2-S NPs and LSW as a reference. The measurements were performed at room temperature using the pendant drop method with a Biolin Scientific Attension Theta Flex Optical Tensiometer. A droplet of crude oil was carefully generated at the tip of a hooked needle within a chamber containing 100 ppm of each individual prepared fluid. The IFT between the oil droplet and the surrounding fluid was recorded over 2000 s. Due to instrument limitations, IFT measurements could not be conducted after the addition of alkali.

2.3.5. Preparation and Characterization of Nanoemulsions. The nanoemulsions were prepared by combining 3 mL of crude oil with 27 mL of nanofluids to create *in situ* oil/water spontaneous emulsions. The mixture was homogenized by gently flipping the vials without using external energy external energy.^{40,53} The nanofluids contained 100 ppm of NPs and 0.1 wt % sodium carbonate (alkali) as optimized concentrations. Detailed procedures for preparing the emulsions and optimizing the concentrations are provided in the Supporting Information (Sections SI4 and SI5).

The objective of this investigation was to evaluate and compare the efficacy of SiO₂-S NPs, SOS-S NPs, and SOS alone in stabilizing *in situ* oil/water emulsions. The stability and characteristics of the emulsions were assessed using visual inspection, droplet size measurement, and microscopic imaging.^{40,53} Initial visual inspections were followed by measurements of the creaming degree (CD %) after 2 weeks of settling.^{76–78} Each sample was prepared and measured three times, and the average value was reported. CD represents the volume fraction of oil separated from the total emulsion volume. A lower CD (approaching 0%) indicates a stable emulsion with minimal oil separation, while a higher CD (near 100%) significant instability.⁷⁶⁻⁷⁸ Particle size distributions were determined at 25 °C using a Malvern MasterSizer 3000 instrument with a Hydro MV dispersion unit. Emulsions were diluted with DW to achieve an obscuration level between 4 and 6%. Measurements were conducted at 1000 rpm with triplicate readings taken for accuracy. Average values were plotted. Microscopic imaging was performed using an Olympus BX51 optical microscope equipped with a digital camera at 50× magnification.

2.4. Enhanced Oil Recovery (EOR) Measurements. 2.4.1. Contact Angle Measurements. Contact angle measurements were conducted to quantitatively evaluate the wettability of the core samples by using a Biolin Scientific Attension Theta Flex Optical Tensiometer. To simulate reservoir conditions, polished sandstone substrates were shaped to fit into a cubic chamber. These substrates were aged in crude oil at 70 °C and atmospheric pressure for 1 week to allow the adsorption of polar crude oil components onto the sandstone surface. This process modified the substrates' wettability to oil-wet conditions.^{75,79,80} After aging, the substrates were dried in an oven at 60 °C for 6 h.^{75,79,80} Wettability was first assessed through oil droplet tests on the sandstone substrates before and after the oil aging process.^{75,79} The oil-aged cores were then immersed in the test fluids for 2 days at 60 °C to simulate prolonged fluid-rock interactions under reservoir conditions.^{75,79} Following the immersion, the substrates were dried again at 55 °C for 2 h to prepare them for contact angle measurements.^{75,79}

During the measurements, an oil droplet was carefully created using a hooked needle and placed on the surface of the substrate immersed in the test fluids.⁷⁵ This allowed for the analysis of the interaction between the sandstone substrate, crude oil, and test fluids, including SOS and nanofluids. The detailed procedure for substrate preparation and contact angle measurement is illustrated in Figure S10a.

2.4.2. Spontaneous Imbibition Test. Prior to the spontaneous imbibition test, a Berea sandstone core plug with diameters of 3.8 and 30 cm in length was sectioned into smaller plugs, each approximately 4.1 cm long. The porosity of these smaller cores was determined at 22 °C using the helium gas expansion technique. The petrophysical characteristics of the core samples utilized in this study are summarized in Table 1.

Spontaneous imbibition tests known for their static natures were conducted to evaluate the performance of the formulated nanofluids for EOR, and to identify the underlying mechanisms. The tests were conducted using high-temperature Amott cells fitted with graduated glass tubes, enabling direct measurement of the oil displaced from the cores.⁷⁵ The oil recovery factor was calculated as the maximum volume of oil recovered over time.^{75,79} All spontaneous imbibition tests were performed without initial water saturation, consistent with the assumptions of the generalized scaling equation.^{75,79} This approach enables direct comparisons across systems by isolating the effects of the nanofluids on wettability alteration and oil displacement mechanisms.⁷⁵ To maintain consistency, all cores were treated under identical conditions, ensuring a reliable comparison of oil recovery among the samples.

The experimental procedure for the imbibition tests is described in detail in our previous work.⁷⁵ Briefly, the cores were saturated with crude oil using a vacuum saturation method and then aged in an oven to alter their wettability to oil-wet conditions.⁷⁵ After being aged, the core surfaces were cleaned with *n*-heptane to remove any excess surface oil. The cores were then placed into the Amott cells, which were filled with the selected concentrations of SOS and nanofluids.

The cells containing the oil-saturated cores and fluids were kept in an oven at 60 $^{\circ}$ C throughout the experiment. The process was continued until no additional oil was recovered. The displaced oil was recorded to calculate oil recovery, expressed as a percentage of the original oil in place (% OOIP), using the following equation:⁵⁰

$$OR = \frac{V_o \rho_o}{M} \times 100\%$$
(1)

OR: represents the percentage of oil recovery after the imbibition test. V_0 : is the volume of oil expelled from the cores. ρ_0 : is the density of oil. *M*: represents the difference in core mass before and after saturation with oil.

2.4.3. Micromodel Flooding Test. The flooding experiments were carried out by using a microfluidic setup to assess the effectiveness of EOR at the pore scale. This method enables direct observation of fluid





Figure 4. (a) Schematic of the micromodel setup. (b) Image of the oil-wet microchip with physical rock networks before and after crude oil saturation.



Figure 5. Pore volume modeling (based on the workflow process illustrated in Figure 1) of fresh sandstone core (a) Sample (1) and (b) Sample (2) for presynthesis process of SiO₂–S NPs and SOS-S NPs.

flow and is more efficient than traditional core flooding tests, as it requires smaller fluid volumes.^{75,81} The microfluidic device provides a real-time visualization of oil recovery, aiding in the identification of mechanisms responsible for oil displacement after the nanofluid flooding.^{81,82} The microchips, along with the chip holder and micromodel connections, were sourced from Micronit, Enschede, The Netherlands. Figure 4 shows the schematic of the experimental setup and the oil-wet microchips with physical rock networks utilized in

this study, which are designed with random rock-shaped structures to closely simulate natural porous media.

The microfluidic setup includes CETONI Nemesys Low pressure with a dual drive system and Harvard PHD 4400 syringe pumps (5 mL capacity), connected to the microchip via poly(tetrafluoroethylene) (PTFE) tubing with 1.6 mm outside diameter and 0.8 mm inside diameter. Ferrules were used at the tubing ends to ensure secure connections and prevent leakage. Effluents were collected through a glass tube attached to the microchip. A Zeiss Stemi 508 microscope, controlled by Zen Light software, was programmed to take scheduled images over a period of 10 h, starting from the beginning of the EOR process. The chip was mounted on a holder, and the system was evacuated using a vacuum pump with the inlet valve closed to remove the air. A 4D valve was employed to prevent air bubbles during fluid injections. The experiment was conducted at room temperature and atmospheric pressure (Figure S6). Initially, LSW was injected followed by crude oil until the effluent collector showed 100% oil stream, establishing initial water and oil saturation. The experiments were conducted with a steady rate of 0.15 μ L/min, equivalent to approximately 1.8 m/day in the oilfield conditions.^{81,82} LSW was used as a secondary oil recovery until no further oil was produced. Then, images were taken to assess and compare the oil recovery and displacement efficiency at the start of EOR tests with the SOS and nanofluids, continuing until no additional oil production was observed. The analysis of microscopic images in oil microchip studies has traditionally relied on tools such as ImageJ and MATLAB for image adjustment and segmentation.⁸³ However, this study employs advanced image processing techniques, demonstrating a robust combination of Python-based technologies and morphological operations to achieve more precise segmentation and quantification. These techniques incorporate advanced statistical modeling and automated image processing workflows, significantly improving the efficacy and scalability of oil distribution analysis over time. Specifically, the use of dynamic thresholding and Gaussian blurring within the OpenCV framework has addressed one of the major challenges reported in previous methods: the reduction of false positives and the enhancement of accuracy in distinguishing oil from other phases. Two key equations were utilized to calculate oil recovery following the flooding with various prepared fluids, as detailed below:

Detected Oil ratio (DOR) =
$$\frac{\text{pixels classified as oil}}{\text{total pixcels in image}}$$
 (2)

$$OR = (1 - DOR) \times 100\% \tag{3}$$

3. RESULTS AND DISCUSSION

3.1. Assessment of Sandstone Reservoir Rock Structure for Presynthesis of Capsule-Shaped SiO₂ NPs. Understanding the pore structure and connectivity of reservoir rocks is essential as it controls the presynthesis and flow behavior of nanofluids, ultimately determining the efficiency of EOR techniques in oil reservoirs.^{61,74,84} Figure 5a,b illustrates the visualization and analysis of the amount and distribution of pores within the microstructure of sandstone reservoir rocks, based on two fresh core samples: Sample (1) and (2), respectively. In this study, advanced three-dimensional visualization technology of digital cores was employed to map accurately the pore space within the target rock samples and locate the distribution of the pore system with precision, as explained in Section 2.2. Each image was segmented using binary image processing to distinguish between pores and the solid rock matrix. The pore space was then classified into connected and disconnected states to reflect the degree of connectivity within the reservoir. In the visual representation, the transparent and colorless areas signify the rock skeleton, while the pore space is divided into three parts: blue (representing detected 2D visualization of pores) and orange

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and yellow (representing the improved 3D pore model for connected pores). The two fresh sandstone samples (1 and 2) were reconstructed using data obtained through CT scanning (Figure 5).

The 3D visualization revealed almost no noticeable differences in pore systems across the reservoir samples. For sandstone reservoir samples, well-developed pores were superimposed and coded with different color labels, indicating a large spatial distribution and better connectivity within the pore network. This is crucial as the proportion of connected pores relative to total porosity is a key factor in determining effective porosity.

This study quantified the ratio of connected to nonconnected pores for the two core samples, which were later subjected to imbibition testing. Sample (1) exhibited a connected pore ratio of $15 \pm 0.38\%$, while sample (2) reached 14.2 $\pm 0.35\%$, with total pore ratios of 21.6 \pm 0.54 and 21.5 \pm 0.53%, respectively. The visibility and distribution of the pores indicate good permeability in these sandstone samples. The interconnected pores can facilitate the injection and movement of enhanced oil recovery agents, such as water, chemicals, or nanoparticles, such as SiO₂. These consistent results confirmed the accuracy of the pore volume fraction calculations. Moreover, the pore and throat radius distributions of both fresh core samples, calculated using the pore network model, are presented in Figure (see Figure 5). The pore throat radii of Samples (1) and (2) ranged from 6.80 to 9.91 μ m, demonstrating minimal variability between the two samples. This uniformity is significant for EOR applications: smaller pores may trap oil, while larger, wellconnected pores facilitate more efficient fluid flow and enhance the displacement of oil by the injected SiO₂ NPs. These findings are critical for optimizing the synthesis of SiO₂ NPs and their subsequent surfactant modification, specifically for EOR applications.

Several key factors were carefully considered:

- (i) SiO_2NPs must be synthesized to align with the detected pore sizes, utilizing techniques such as sol-gel processing.^{60,69} Adjusting reaction conditions will allow for the synthesis of SiO₂ NPs, including their functionalized forms, with controlled size distribution and appropriate shapes targeting the mean pore sizes (6.80 and 9.91 μ m). This ensures that the NPs avoid pore blockage and contribute to effective oil displacement.
- (ii) The shape of the NPs also plays a critical role in their ability to navigate through reservoir pores. Targeting capsule-shaped SiO₂ NPs offers potential advantages, as these are proposed to align directionally with the pore structures, thereby optimizing oil displacement.

Smaller pores, in particular, may benefit from SiO₂ NPs that alter the wettability of the rock, increasing water-wetness and improving oil recovery. The following section will provide a detailed overview of the synthesis, optimization, and surfactant functionalization process of SiO₂-S NPs with SOS, based on the comprehensive analysis of pore sizes and matrix structures within the sandstone rock samples.

3.2. Characterization Studies for Nanoparticles. 3.2.1. Morphology and Surface Area Measurement. The SEM analysis was initially employed to determine the optimal dodecanol concentration required to achieve synthesized capsule-shaped NPs. The SiO₂-S20 NPs (synthesized with 1 mg/mL dodecanol) displayed early indications of capsule morphology, as shown in Figure S1a. However, a substantial



Figure 6. SEM images of (a, b) the unmodified SiO₂-SNPs and (c, d) SOS-NPs.



Figure 7. (a) TGA thermograms and (b) FTIR spectroscopy in the framework regions 400–4000 cm⁻¹, for SiO₂–SNPs and SOS-S NPs.

proportion of the particles retained a spherical form. Increasing the dodecanol concentration to 1.5 mg/mL resulted in a marked improvement, yielding predominantly capsule-shaped NPs, as illustrated in Figures 6a,b, and S1b. The sample synthesized with 30 mg of dodecanol was selected for the subsequent functionalization with SOS surfactant based on these SEM images. Figure 6c,d, along with Figure S1b show the SEM images of the SOS-S NPs, demonstrating that the capsule shape of the SiO₂-S NPs was preserved after functionalization. The average particle size was 188.2 ± 17 nm (with an average surface area of 29846 ± 266 nm²) for SiO₂-S NPs and 97.8 ± 14 nm (with an average surface area of 11713 ± 189 nm²) for SOS-S NPs. The



Figure 8. Chemical structure scheme depicting (stage 1) the synthesis of SiO_2 -S NPs and (stage 2) their functionalization with SOS surfactant, including the associated chemical reactions and functional groups.

EDX spectra for different samples are depicted in Figure S7. The spectrum of the unmodified SiO_2-S NPs displays peaks corresponding to silicon and oxygen, reflecting the expected composition of unmodified SiO_2-S NPs. After functionalization, the SOS-S NPs spectrum showed a reduced silicon signal, increased oxygen, and the appearance of sodium. These changes indicated the successful attachment of the SOS surfactant to the surface of the SiO₂-S NPs, confirming the effectiveness of the surface modification process.

The textural characteristics of the SiO₂–S NPs, before and after functionalization with SOS were assessed using BET analysis. The BET surface area of unmodified SiO₂–S NPs measured at 274 ± 11 m²/g, decreased significantly to 89 ± 4 m²/g following SOS functionalization. This considerable reduction in surface area can be attributed to SOS surfactant coverage on the SiO₂–S NPs surfaces, potentially impeding the adsorption and diffusion of N₂ molecules into the internal pore structure.

3.2.2. TGA Analyses and Functionality Assessment. The TGA analyses of the synthesized SiO₂-S NPs before and after grafting SOS provided critical insights into the thermal stability, decomposition behavior, and quantification of SOS content on the surface of the SiO₂-S NPs. The TGA curves presented in Figure 7a indicate that both samples exhibited an initial weight loss at relatively low temperatures (50 to 200 °C), likely due to moisture loss or surface dihydroxylation. Notably, thermal degradation profiles differ significantly between the two samples, reflecting the impact of functionalization on the thermal properties of the SiO₂-S NPs. For the SiO₂-S NPs, a gradual weight loss begins around 200 °C, with a more pronounced decline observed between 200 and 400 °C. This weight loss is attributed to the decomposition of residual organic materials or unreacted precursors within the SiO₂-S NPs matrix. The weight stabilized at around 72% of the initial mass, indicating that the majority of the material remained thermally stable beyond 400 $^{\circ}$ C, with an overall weight loss of approximately 28 ± 2.5%. By contrast, SOS-S NPs exhibited a different thermal degradation

pattern, characterized by significant weight loss between 200 and 650 °C. This degradation was primarily attributed to the decomposition of the organic SOS surfactant grafted onto the surface of the SiO₂-S NPs. The TGA curve for the SOS-NPs stabilized at a lower residual weight of approximately 45%, corresponding to a weight loss of about $55 \pm 1.3\%$, highlighting the substantial contribution of the organic surfactant to the overall mass of the NPs. These results confirmed the successful grafting of the SOS surfactant onto the surface of the SiO₂-S NPs.

Further confirmation of successful SOS functionalization on the SiO₂-S NPs was provided by FTIR spectroscopy. The FTIR spectra of both the SiO_2 -S and SOS-S NPs, as shown in Figure 7b, revealed key differences. The spectrum of the unmodified SiO₂-S NPs displayed characteristic vibrational bands associated with the silica network, including prominent Si-O-Si asymmetric stretching vibration around 1100 cm⁻¹ and another near 800 cm^{-1.85} Peaks around 470 cm⁻¹ were attributed to the Si-O bonds.^{85,86} Following SOS functionalization, the FTIR spectrum of SOS-S NPs showed the appearance of new peaks, notably in the 2950-2850 cm⁻ region, corresponding to C-H stretching vibrations.⁸⁷⁻⁸⁹ These bands provided strong evidence of the presence of the alkyl chains from the SOS surfactant on the silica surface. Additionally, a peak observed around 1200 cm^{-1} , associated with S=O stretching vibrations, was indicative of the sulfonate group within SOS.⁹⁰ These spectral changes provided clear evidence for the successful grafting of SOS onto the SiO₂-S NPs, confirming effective surface functionalization.

The FTIR results strongly support the functionalization of SiO₂ NPs with SOS surfactant molecules. Key observations included the appearance of characteristic S=O stretching (~1200 cm⁻¹) and C-H stretching (~2900 cm⁻¹) vibrations in the SOS-S spectrum, which were absent in the SiO₂-S spectrum. These features, coupled with shifts in the Si-O-Si peaks, suggested significant interaction between the SiO₂ surface and the SOS surfactant molecules. Although the absence of a distinct

O-C peak might seem counterintuitive for grafting, it is wellestablished that such bonds often produce weak and overlapping signals that can be dominated by the intense Si-O-Si and Si-O peaks in SiO₂-based systems. The differences observed between the spectra of SOS-S and the pure SOS solution where S=Ostretching and C-H stretching also appeared at ~1200 and \sim 2900 cm⁻¹, respectively, (see Figure S8) further validated that the SOS surfactant was immobilized on the SiO₂ surface, altering their vibrational characteristics. This alteration ruled out ordinary physical mixing, as simple composites did not exhibit such spectral changes. These findings aligned with previous studies, which emphasized the importance of indirect evidence, such as peak shifts and the emergence of new functional group signals, in confirming grafting in complex systems.^{91,92}

Based on TGA and FTIR analyses, it can be concluded that the SOS-S material represents a chemically functionalized system rather than a simple physical mixture.

When synthesized, capsule-shaped SiO₂-S NPs were modified with SOS molecules, which acted as a stabilizing agent. The modification could involve both covalent and noncovalent interactions, depending on the specific reactions and the interaction of SOS with the SiO₂-S NPs surface. For instance, the negatively charged sulfonate group (SO_3^{-}) in SOS could interact with positively charged sites on the SiO₂-S NPs surface, such as $(Si-OH_2^+)$. Additionally, the hydrophobic alkyl chain of SOS could interact with residual organic species (from dodecanol) that are absorbed on the SiO₂-S NPs surface as well as with hydrophobic regions within the NPs. Moreover, the (Si–OH) on the SiO₂-S NPs surface may form hydrogen bonds with the oxygen atoms in the (SO_3^{-}) of SOS in the presence of water molecules. In functionalization protocols involving the reaction of SOS with activated (Si-OH₂⁺), covalent bonding between SOS and the SiO₂-S NPs surface could also occur. The chemical structure scheme in Figure 8 illustrates the two stages of SiO₂-S NPs preparation and functionalization with SOS surfactant, depicting the expected chemical reactions and functional groups responsible for these interactions based on the natural properties of the chemicals used in this study.

3.3. Characterizations of Nanofluids. 3.3.1. Zeta Potential Measurements and Size Distribution. ZP is a critical parameter for determining the surface charge and stability of NPs. High absolute ZP values (ZP > +30 mV or ZP < -30 mV) indicate strong electrostatic repulsion between particles, reducing aggregation and improving stability.⁹³ Conversely, NPs with low ZP values (-30 < ZP < +30 mV) are less stable, due to weaker electrostatic repulsion, allowing attractive forces to dominate and causing aggregation.93 This instability can hinder the effectiveness of NPs in EOR applications.⁹⁴ Surface modification with surfactants is an effective strategy to enhance NPs stability by preventing aggregation.^{37–40}

The ZP values of 100 ppm of the synthesized SiO₂-S NPs, before and after functionalization with the SOS, are illustrated in Figure 9. Functionalization with SOS increased the ZP from approximately -11 ± 0.1 to -46 ± 0.3 mV, indicating enhanced stability. The addition of 0.1 wt % alkali (N2) further improved the ZP, increasing it to -27 ± 0.4 mV for SiO₂-S NPs and -56 \pm 0.4 mV for SOS-S NPs (see Figure 9). This improvement can be attributed to the deprotonation of the Si-OH surface groups under alkaline conditions, leading to the formation of more Si-O⁻ groups. These negatively charged groups increase electrostatic repulsion between particles, preventing aggregation and enhancing dispersion stability.



Figure 9. ZP analyses of SiO₂-SNPs and SOS-S NPs without (N1) and with alkali (N2).

Figure S9 shows the size distribution of 100 ppm of SiO_2-S NPs and SOS-S NPs in nanofluid formulations without (N1) and with alkali (N2). SOS functionalization reduced the particle size of SiO₂-S NPs from 237 ± 6.7 to 80 ± 4.2 nm. The addition of alkali further decreased the particle sizes to 162 ± 5 nm for SiO₂–S NPs and 55 \pm 2.7 nm for SOS-S NPs. These reductions in particle sizes indicate enhanced dispersion stability, as smaller sizes reflect reduced aggregation. It is worth noting that the hydrodynamic particle sizes are smaller than those observed from microscopy analysis, presumably due to the particle shape. Capsule-shaped particles can have higher diffusion coefficients along their short axis compared to spheres, which can influence the size obtained from DLS measurements.

The results confirm that SOS functionalization and alkali addition work synergistically to improve nanofluid stability. This approach ensures better dispersion and functionality, particularly in the presence of alkali, as suggested in prior studies.⁵³

3.3.2. IFT Measurement. Figure 10 presents the IFT measurements between crude oil and various prepared fluid. The measurements were conducted as a function of time,



Figure 10. IFT measurements between crude oil droplets and various prepared fluids.



Figure 11. Spontaneous emulsification comparing alkali, 100 ppm of SiO₂–S NPs, SOS, and SOS-S NPs at (a) day 0 and (b) after 2 weeks of aging. (c) The creaming degree (CD %) of the emulsions after 2 weeks.

providing insights into the dynamic interfacial behavior of LSW and different nanofluids in contact with the crude oil.

LSW exhibited the highest IFT at approximately 24 ± 0.2 mN/m with a slight decrease over time, indicating a minimal interaction with the oil—water interface. The use of SiO₂–S NPs reduced the IFT to 16 ± 0.1 mN/m, likely due to NPs adsorption at the interface.

Introducing 100 ppm of SOS surfactant alone further reduced the IFT to 10 ± 0.1 mN/m, demonstrating its strong surface activity. The most significant reduction was achieved with 100 ppm of SOS-S NPs (containing 27 ppm of SOS based on TGA analysis). The IFT dropped to 1.3 ± 0.01 mN/m, demonstrating the synergistic effect between SiO₂-S NPs and SOS.

It is worth noting that all of the measurements were conducted without alkali due to instrument limitations, as the device cannot measure very low IFT values. When 0.1 wt % alkali was added to 100 ppm of SOS-S NPs, the oil droplet could not be formed, suggesting an IFT in the range of 10^{-2} to 10^{-4} mN/m. This substantial reduction indicates the formation of a stable interfacial film.

These findings demonstrate that functionalizing SiO₂-S with SOS significantly reduces IFT while minimizing surfactant use. This grafting approach achieved ultralow IFT values at low surfactant concentrations, reducing chemical consumption and making the process both cost-efficient and environmentally friendly. These attributes are critical for practical EOR applications.

3.4. Characterization Studies for Nanoemulsions. *3.4.1. Investigation of Spontaneous Emulsification and Stability of SOS-S NPs in Oil/Water Systems.* Spontaneous oil-in-water emulsification has been identified as a crucial mechanism in EOR applications.^{53,54,95} In this study, different oil-water emulsions were prepared to evaluate the ability of the synthesized nanofluids to generate spontaneous *in situ*

emulsions. Figure 11a,b presents the emulsification behavior of SiO₂-S NPs and SOS-S NPs compared to alkali and SOS alone over a two-week aging period. The inclusion of alkali and unmodified SiO₂-S NPs resulted in slight color changes in the emulsions, indicating some level of emulsification. However, more pronounced changes were observed with SOS, and even more so with SOS-S NPs. Oil separation was visible in all samples. However, the SOS-S NPs emulsion retained more dispersed oil within the water phase and showed significantly less oil accumulation at the top (Figure 11b). This indicates that SOS-S NPs are the most effective in maintaining emulsion integrity over time. The CD % was calculated after 2 weeks of aging in order to quantify the stability of the generated emulsions, as shown in Figure 11c. The SOS-S NPs exhibited the lowest CD %, outperforming both unmodified SiO₂-S NPs and SOS alone. These results demonstrate the effectiveness of grafting SOS onto SiO₂-S NPs in enhancing the stability of oilin-water emulsions and highlight their potential for EOR applications.

3.4.2. Droplet Size Distribution of Emulsions. The spontaneous formation of emulsions within porous media plays a crucial role in facilitating efficient fluid flow at the pore scale, making it valuable for the EOR during chemical flooding. Emulsions with smaller droplet sizes are especially advantageous, as these can more readily penetrate micropores, leading to improved sweep and displacement efficiency.^{53,96} Figure 12a-c shows the average droplet size distribution of emulsions formed by 100 ppm of SiO₂-S NPs and SOS alone (without the addition of alkali). It should be noted that size distribution measurements with alkali were inconclusive due to the dilution required for analysis with the MasterSizer. Consequently, only the measurements obtained through microscopic imaging are reported, as depicted in Figure 12d-f.



Figure 12. Average droplet size distribution of emulsions generated with 100 ppm of (a) $SiO_2 - SNPs$, (b) SOS alone, and (c) SOS-SNPs. Microscopic images of oil droplets formulated in the presence of alkali using (d) $SiO_2 - SNPs$, (e) SOS, and (f) SOS-SNPs.

MasterSizer analysis revealed a significant reduction in oil droplet size with SOS-S NPs, compared to those with both SiO_2-S NPs and SOS alone. The grafted SiO_2-S NPs produced emulsions with notably smaller droplet sizes. By contrast, using surfactant alone or SiO_2-S NPs resulted in larger droplet sizes, which could pose challenges during injection, particularly in reservoirs with small pore sizes.⁴² The smaller droplet sizes observed in the presence of SOS-S NPs are advantageous for EOR applications, as these can effectively penetrate micropores within the porous media, thereby improving sweep efficiency and oil displacement. These findings demonstrated the potential of SOS-S NPs to optimize fluid flow, primarily due to their role as nanocarriers for surfactants, which facilitates the formation of emulsions with smaller droplet distributions. Additionally,

microscopic imaging was used to analyze droplet formation across the different emulsification systems. Figure 12d–f illustrates the oil droplets formed using SiO₂–S NPs, SOS, and SOS-S NPs in the presence of alkali. The microscopic images reveal noticeable differences in the droplet size and distribution across the three emulsification systems. Figure 12d shows large and nonuniformly distributed droplets with SiO₂–S NPs, indicating poor emulsification, possibly due to insufficient stabilization. By comparison, the addition of the SOS surfactant produced smaller droplets compared to SiO₂–S NPs; however, the droplet sizes remained relatively large for systems requiring penetration into small pore spaces. From Figure 12f, it can be qualitatively observed that the application of SOS-S NPs led to a



Figure 13. Contact angle measurements of (a) SiO₂-S NPs, (b) SOS, and (c) SOS-NPs. (d) Average of the static contact angle measurements for each system.

significant improvement, producing very fine droplets, indicating effective droplet stabilization in the presence of these NPs.

These results suggest that grafting SOS onto SiO_2 -S NPs significantly enhanced their ability to produce smaller and more stable oil droplets, which is essential for optimizing fluid flow at the pore scale during EOR application.

3.5. EOR Measurement. *3.5.1. Contact Angle Measurement.* The contact angle measurement is a fundamental technique for evaluating surface wettability and characterizing the interactions at the interface of different phases.⁷⁵ Natural reservoirs are generally water-wet; however, they can shift to oilwet conditions due to the deposition of heavier hydrocarbons on rock surfaces.⁹⁷ Wettability classification is typically based on contact angles measured with respect to the denser phase (water): water-wet (0–75°), intermediate-wet (75–105°), and oil-wet from (105–180°).^{75,97}

This study focuses on evaluating the capability of nanofluids to alter the wettability of rock surfaces from oil-wet states to water-wet states. In this work, the contact angle was obtained using a Biolinc Scientific Attension Theta Flex optical tensiometer, which measures angles relative to the less dense phase (oil). Following Anderson's approach, the equivalent contact with respect to the denser phase can be estimated by subtracting the measured value from 180° .^{75,79,98} Under this convention, contact angles exceeding 90° indicate water-wet conditions, whereas angles below 75° represent oil-wet conditions.^{75,79,98} Figure S10b illustrates the contact angle measurements conducted before and after the aging process. The findings demonstrate a significant change in wettability with the substrate shifting from water-wet to strongly oil-wet after aging. This alteration is likely due to the partial adsorption of polar crude oil components onto the sandstone surface, modifying its surface characteristics.

Further contact angle measurements were performed at room temperature using surfactant and nanofluid treatments, as shown in Figure 13. The SOS surfactant alone produced a contact angle of $120^{\circ} \pm 1.5$, indicating a water-wet state. SiO₂-S NPs alone exhibited limited efficacy in altering wettability, with a contact angle of approximately $20^{\circ} \pm 0.1$. In contrast, SOS-S NPs achieved a significant increase in the contact angle to $173^{\circ} \pm 1.3$, corresponding to a strongly water-wet condition.

These results demonstrate the enhanced efficacy of SiO_2-S NPs in modifying wettability compared with individual treatments with either surfactant or nanoparticles. This approach presents a promising strategy for achieving the targeted wettability alteration in EOR applications.

3.5.2. EOR in Oil-Wet Sandstone Cores. 3.5.2.1. Spontaneous Imbibition Test. Figures 14 and S10 present the results of the spontaneous imbibition test conducted on oil-wet sandstone cores over a twenty-day period to evaluate the EOR performance of synthesized SiO₂-S NPs alone, SOS, and SOS-S NPs. The oil recovery percentage was plotted against time, allowing for a comparative analysis of the efficacy of each treatment. The unmodified SiO₂-S NPs exhibited the lowest oil recovery,



Figure 14. Oil recovered percentage from saturated cores over time during spontaneous imbibition test using different prepared fluids.

stabilizing around 35 ± 0.7% and reaching a plateau by approximately Day 5. This limited recovery is likely due to their low stability and insufficient capacity to alter the wettability of the rock surface effectively. By contrast, the application of the SOS alone resulted in an approximate 7% increase in oil recovery over SiO₂–S NPs, stabilizing at around 42 ± 1% and plateauing by Day 7. The surfactant likely adsorbed onto the rock surface, leading to a change in the wettability of the core surface to the water-wet state. This wettability alteration promoted the detachment of oil from the rock surface, thereby enhancing oil displacement by water. The SOS-S NPs demonstrated the highest oil recovery, reaching around 77 ± 1.5%, with recovery plateauing around Day 10. Functionalizing SiO₂–S NPs with SOS significantly enhanced their ability to modify the rock

surface from oil-wet to strongly water-wet, as confirmed by contact angle measurements. This functionalization not only altered the wettability but also led to the spontaneous formation of smaller and more stable oil-in-water emulsions, which potentially contributed to the improved mobilization and recovery of oil. Smaller droplets are more capable of displacing through the pore network of the core, reducing the possibility of blockages that can occur with larger oil droplets. This pronounced improvement of oil recovery can be attributed to the synergistic effect of the SOS-S NPs in both altering wettability and facilitating the formation of spontaneous emulsion. As demonstrated in Figure S12, the oil droplets on the surface of the core treated with SOS alone were significantly larger than those on cores treated with SOS-S NPs. This indicates that the improved stability and dispersibility of functionalized SiO₂-S NPs, are critical for better oil recovery. Additionally, this functionalization reduced the required concentration of SOS compared to the application of surfactant alone, highlighting their significant role in optimizing surfactant usage and thereby making the process more cost-effective.

3.5.2.2. Postassessment of Sandstone Core Samples after Spontaneous Imbibition Testing of Injection Fluids. After conducting imbibition tests on the synthesized and functionalized SiO₂-S NPs, the microstructures of core samples (1) and (2) were further analyzed using CT scanning, as depicted in Figure 15. Notably, the core sample (2), which was injected with SOS-S NPs, exhibited the widest pore distribution, indicating superior pore connectivity. In contrast, the core sample (1), subjected to SiO₂-S NPs during the imbibition test, demonstrated the narrowest pore distribution, signifying the poorest connectivity. Interestingly, the pore volume in SiO₂-S NPs saturated sample (1) was observed to be lower than that of SOS-S NPs saturated sample (2), indicating a significant reduction in the permeability between the two tested samples. Further, the postimbibition analysis of cores revealed substantial differences



Figure 15. Pore volume modeling (based on the workflow process illustrated in Figure 1) after imbibition testing of injected (a) SiO_2 -S NPs and (b) SOS-S NPs, through fresh sandstone core samples (1) and (2), respectively.

between the two samples in terms of the connected pore volume. Specifically, as depicted in Figure 16, sample (2) exhibited a



Figure 16. Pore connectivity analysis of fresh and tested (saturated) core samples.

higher proportion of connected pores, reaching $9.8 \pm 0.24\%$, compared to sample (1), which showed a connected pore proportion of $6.2 \pm 0.15\%$. This signifies that pore connectivity in fresh sample (1) decreased by 58.7%, while fresh sample (2) experienced a reduction of 30.9% following imbibition testing with SiO₂-S and SOS-S NPs, respectively (see Figure 16). These findings align well with the oil recovery percentages observed during spontaneous imbibition tests conducted on saturated Berea sandstone cores using two different imbibition fluids.

The results indicate that although the capsule-shaped SiO_2 NPs provide a moderate increase in surface area for interaction at the water—oil interface, leading to a slight reduction in interfacial tension (IFT), and enhanced oil displacement, their limited wettability may prove beneficial under specific conditions. Capsule-shaped SiO_2 NPs can be utilized to selectively plug high-permeability zones, redirecting injected water and chemicals into less permeable areas and thereby mobilizing more trapped oil. Moreover, surface functionalization of these capsule-shaped SiO_2 NPs with hydrophilic groups can further improve their dispersion in water-based EOR fluids, facilitating better interaction with oil-wet sandstone surfaces.

Herein, when capsule-shaped SiO_2 NPs were functionalized with SOS surfactant, the performance of the injected fluids was enhanced by increasing wettability alteration, reducing IFT, and stabilizing oil-in-water emulsions. Consequently, this improved the overall efficiency of the oil recovery. These findings are consistent with the observations from the spontaneous imbibition tests involving the injected fluids, further supporting the role of functionalized SiO_2 NPs in improving EOR outcomes.

3.5.3. EOR by Micromodel Flooding Test. Micromodel flooding tests conducted on oil-wet microchips provided critical insights into fluid flow dynamics within porous media, allowing for direct visualization and a more detailed understanding of the mechanisms responsible for EOR compared to traditional core flooding tests.^{75,82,83} These tests also evaluated the efficacy of various nanofluids in EOR. Accordingly, the experiments started with sequential flooding using LSW for secondary oil recovery, followed by the injection of surfactants and nanofluids. Figure 17



Figure 17. Tertiary oil recovery rates over time as determined through microfluidic flooding tests for the different prepared samples.

shows the oil recovery over time for microchips treated with different prepared samples. The SiO₂-S NPs exhibited the lowest recovery rate, around $18 \pm 1\%$. This low recovery rate can likely be attributed to the limitations of these NPs in altering surface wettability as well as their low stability, which hindered efficient oil displacement. In contrast, flooding with the SOS surfactant alone achieved a recovery rate of around $38 \pm 1.2\%$, which subsequently plateaued, demonstrating the surfactant's effectiveness in modifying the microchip's wettability. For the SOS-S NPs, the recovery rate increased significantly, reaching approximately 83%, and stabilizing at around 86 \pm 2.5%. This substantial improvement in oil recovery can be attributed to the effective wettability alteration induced by SOS-S NPs. Additionally, the functionalization of SiO₂-S NPs with SOS surfactant enhanced the interaction between the NPs and the oil-wet surface, facilitating oil displacement and promoting the formation of smaller, more stable oil-in-water emulsions. This increase in oil recovery, approximately 48% over surfactant flooding, is linked to the generation of smaller oil droplets, as illustrated in Figures 18 and S11. Table S1 provides videos of the microchips during the flooding tests, illustrating the behavior of different fluids over time.

3.5.4. Proposed Mechanisms and Efficacy of SOS-S NPs in EOR from Oil-Wet Porous Media. Figure 18 illustrates the proposed mechanisms for EOR using SiO₂-S NPs, SOS, and SOS-S NPs during injection into oil-wet porous media. The application of unmodified SiO₂-S NPs resulted in the lowest oil recovery in both the spontaneous imbibition test and the microchip test. This low recovery is attributed to the nanoparticles' limited ability to alter the surface wettability from oil-wet to water-wet as well as their low stability (see Figure 18a). The emulsion blockage, particularly by large individual oil droplets, is a critical concern in porous media, depending on the relative sizes of the emulsions and the pores.⁹⁹ This issue is particularly relevant to EOR applications. In this study, the use of SOS surfactant alone for EOR showed superior wettability alteration and higher oil recovery compared to that of the unmodified SiO₂-S NPs. However, its application also led to the formation of larger oil droplets, which have the potential to obstruct pore channels, as illustrated in Figure 18b. The application of SOS-S NPs demonstrated enhanced interaction with crude oil, which is characterized by the spontaneous in situ



Figure 18. Suggested mechanisms for EOR using (a) SiO₂-S NPs, (b) SOS, and (c) SOS-S NPs.

Table 2. Comparison	of Characteristics	s of NPs and T	Their Associated	EOR Efficiency	of Most Effective	Silica NPs

			characteristi	EOR				
sample	shape	average particle size (nm)	ZP (mV)	contact angle (deg)	IFT (mN/m)	imbibition testing	flooding testing	ref
SiO ₂ NPs	spherical	104	-	73	4	-	32	60
SiO ₂ NPs	spherical	35	-	79	9	-	38	81
SiO ₂ NPs	spherical	187	-	18	-	-	17	103
ZnO/SiO ₂ /Xanthan	near spherical	74-138	-31	130	6	34	-	10
SiO ₂ NPs	spherical	30	-	-	-	27	39	102
SiO ₂ -PEI NPs	spherical	56	45	16	5	10	-	75
SiO ₂ -TOS NPs	spherical	62	-40	165	19	65	-	75
SiO ₂ –S NPs	capsule	188	-11	20	16	35	18	this work
SOS-S NPs	capsule	98	-46	173	$10^{-2} - 10^{-4}$	77	86	this work

formation of stable emulsions. This effect is due to the dual affinity of this nanofluid for both water and oil, which led to significant wettability alteration of the porous surface to a waterwet state, as confirmed by contact angle measurements. Moreover, the application of SOS-S NPs resulted in a significant reduction in IFT, even at lower concentrations of SOS compared to the use of SOS alone, as evidenced by TGA and IFT analyses. The spontaneous formation of smaller, more stable emulsion droplets, observed through microscopic images and MasterSizer analysis, increased the contact area between the oil and the porous media surfaces. This enhanced interaction facilitated a deeper penetration into the rock matrix, reducing the likelihood of oil trapping and leading to improved oil displacement and recovery (see Figure 18c).^{100,101} Additionally, the introduction of an alkaline environment further improved the stability of SOS-S NPs and contributed to an additional IFT reduction. It is important to note that the effectiveness of these proposed mechanisms is influenced by various factors, including the stability of the nanofluids, the properties of the reservoir, and the type of crude oil used.^{53,54,101} In conclusion, the synthesized

SOS-S NPs nanofluid showed promising results for EOR applications by altering rock wettability, reducing IFT, and promoting the formation of spontaneous stable oil-in-water emulsions. These effects enable deeper penetration and mobilization of the trapped oil. However, further investigations and research under varying reservoir conditions, such as high salinity and elevated temperatures, along with field-scale applications, are essential to validate and optimize these approaches for practical implementation in the future.

Despite the general effectiveness of highly uniform spherical NPs in reducing IFT and altering wettability as reported in the literature. ^{10,51,60,75,81,102,103} It was crucial to compare the results of this study with the relevant literature to identify the optimal performance of spherically shaped SiO₂ for EOR. Table 2 summarizes a comparative analysis of properties and EOR performance among spherical SiO₂, capsule-shaped SiO₂-S, and SOS-S. Key metrics analyzed included particle size, ZP, contact angle, IFT, imbibition testing, and micromodel flooding for EOR efficiency.

The SiO₂ NPs in the comparison varied in size from 30 to 187 nm, while the capsule-shaped SiO₂-S had a size of approximately 188 nm. Notably surface modification of both spherical and capsule-shaped SiO₂ NPs led to significant reductions in particle size and substantial increases in contact angle, indicating waterwet properties, potentially beneficial in altering rock wettability for oil recovery. Additionally, surfactant modifications significantly reduced the IFT values, underscoring their enhanced potential for IFT reduction and oil mobility improvement compared to those of SiO₂-S (16 mN/m) and spherical SiO₂ (4-20 mN/m). The capsule-shaped SOS-S NPs, with smaller particle sizes (~98 nm) and high uniformity, exhibited superior dispersion in solution, effective wedge film formation, and stronger interaction with solid surfaces, potentially resulting in enhanced wettability alteration and improved EOR performance. These findings align well with the results of this study. In the spontaneous imbibition test, the SOS-S achieved an EOR efficiency of 77% doubling the recovery observed with SiO₂-S NPs (35%) and spherical SiO₂ NPs (10-34%). These results were confirmed by micromodel flooding tests, where the SOS-S NPs demonstrated an outstanding EOR efficiency of 86%, which was significantly higher than SiO_2 -S NPs (18%) and traditionally spherical SiO₂ NPs (17-39%). Moreover, spherical SiO₂ NPs had a wide contact angle range of $18-79^\circ$, while SiO₂-S had a contact angle of 20°. However, SOS-S had a very high contact angle of 173°, which implied water-wet properties, potentially beneficial in altering the rock wettability for oil recovery. Also, SOS-S NPs exhibited the lowest IFT ($\sim 10^{-2} - 10^{-4} \text{ mN/m}$), suggesting superior ability to reduce IFT and improve oil mobility compared to SiO_2 -S (16 mN/m) and spherical SiO₂ (4-19 mN/m). Additionally, the SOS-S NPs' high uniformity would lead to better dispersion in solution, well-ordered wedge film, and stronger interaction with the solid surface that could result in more efficiency in wettability alteration.

4. CONCLUSIONS

This study presents a comprehensive evaluation of capsuleshaped silica NPs functionalized with SOS surfactant for EOR in oil-wet sandstone reservoirs. Characterization results confirmed successful functionalization and its impact on NPs properties. SEM analyses confirmed the preservation of capsule-shaped morphology following the functionalization with SOS, while the particle size decreased significantly from 188 \pm 15 to 98 \pm 14 nm. EDX results verified SOS grafting through the appearance of sodium, while TGA analyses revealed a 55% weight loss in SOS-S NPs compared to 28% for SiO₂–S NPs, indicating substantial SOS presence. FTIR analyses showed distinct sulfonate and alkyl group peaks at 1200 and 2950–2850 cm⁻¹, confirming surface modification.

ZP measurements demonstrated enhanced stability, with values increasing from -11 ± 0.1 mV for SiO₂–S NPs to -46 ± 0.3 mV for SOS-S NP. The addition of 0.1 wt % alkali further improved stability, increasing ZP values by approximately -10 mV. The IFT between crude oil and SOS-S NPs was reduced from 24 to 1 mN/m, with further reductions estimated upon the addition of alkali.

Nanoemulsion characterization further highlighted the role of SOS-S NPs in EOR. SOS-S NPs exhibited the lowest CD %, indicating superior emulsion stabilization compared to SiO₂–S NPs and SOS alone. Microscopic imaging confirmed that SOS-S NPs facilitated the formation of smaller droplets compared with SOS and SiO₂–S NPs, enhancing fluid flow and sweep efficiency.

Contact angle measurements showed a shift from $20^{\circ} \pm 0.1$ (oil-wet) to $173^{\circ} \pm 1.3$ (strongly water-wet), demonstrating effective wettability alteration using SOS-S NPs. Performance tests validated the effectiveness of SOS-S NPs, with spontaneous imbibition tests recorded oil recovery of $77 \pm 1.5\%$, outperforming SOS alone ($42 \pm 1\%$) and SiO₂-S NPs ($35 \pm 0.7\%$). Micro-CT analyses revealed a reduction in pore connectivity to 59% in cores treated with SiO₂-S NPs, compared to 31% for SOS-S NPs. This indicates improved pore accessibility with SOS-S NPs. Micromodel flooding tests confirmed these findings, achieving $86 \pm 2.5\%$ oil recovery with SOS-S NPs, compared to $38 \pm 1.2\%$ with SOS and $18 \pm 1\%$ with SiO₂-S NPs.

In conclusion, SOS-S NPs enhance oil recovery through IFT reduction, wettability alteration, and nanoemulsions stabilization. Furthermore, their effectiveness at lower concentrations compared to the higher concentrations typically required for surfactants alone highlights their efficiency. The relative simplicity of the synthesis and functionalization processes supports the scalability of this approach for industrial applications. Future research should investigate their performance under diverse reservoir conditions and crude oil types as well as assess their environmental compatibility and large-scale production feasibility.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.energyfuels.4c05018.

Experimental and optimization methods, characterization data, spectra, additional figures, and supplementary tables (PDF)

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Notes

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