

Original Paper

In situ-generated silica nanonetworks for energy-efficient enhanced oil recovery: Breaking the migration–aggregation dilemma in heterogeneous reservoirs



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ABSTRACT

Maximizing energy efficiency in hydrocarbon extraction remains hampered by water channeling in heterogeneous reservoirs, where conventional pre-synthesized nanoparticles often fail due to the unresolved migration–aggregation dilemma. We report a novel strategy that addresses the long-standing migration–aggregation dilemma of pre-synthesized nanoparticles by enabling the *in situ* formation of functional silica nanonetworks directly within reservoir pore throats. Our approach employs a tetraethyl orthosilicate (TEOS) emulsion that, upon controlled demulsification, undergoes hydrolysis and condensation to generate silica nanoparticles *in situ*. Glycerol mediates dielectric tuning and modulates nanoparticle zeta potential, allowing precise control over particle size and distribution to match medium-to-high-permeability zones (100–1000 mD). Displacement experiments demonstrate exceptional performance, achieving a water shutoff efficiency of over 90% while retaining more than 70% of oil-phase permeability. Mechanistic studies reveal that surfactants released during demulsification play a dual role. They enhance silica nucleation rate by reducing the interfacial energy barriers and adsorb onto nanoparticle surfaces, conferring strong hydrophobicity for selective water shutoff. Furthermore, the *in situ*-generated SiO₂ nanoparticles form a stable three-dimensional plugging network through physical bridging, aggregation, and surfactant-mediated anchoring on rock surfaces. Compared to conventional high-viscosity systems, the ultra-low viscosity and *in situ* formation strategy of this system results in lower operational energy consumption. This strategy improves nanoparticle delivery efficiency and provides an energy-efficient approach for enhanced oil recovery.

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1. Introduction

It is critical to maximizing recovery from existing oil reservoirs in the context of growing global energy demand and the imperative for a sustainable energy transition. However, a major challenge in mature and heterogeneous reservoirs is ineffective water circulation, where injected water preferentially flows through high-permeability channels, bypassing oil-rich zones. This phenomenon not only limits oil recovery but also represents a significant source of energy waste, reducing the overall energy efficiency of the extraction process

(Fig. 1) (Guo et al., 2022; Seright and Brattekas, 2021; Wang et al., 2024a). Conventional water shutoff technologies, such as polymer gels and inorganic agents, often suffer from drawbacks like low strength, thermodynamic instability, and poor in-depth migration capacity, limiting their efficacy in nano-to micro-scale pore throats and fractures (Chen et al., 2023; Kang et al., 2021; Yin et al., 2022). Therefore, developing advanced water shutoff systems with high selectivity, deep migration capability, and reservoir adaptability is paramount for improving oilfield recovery efficiency.

Nanomaterials offer promising solutions for enhanced oil recovery (EOR) (Khalil et al., 2017; Lv et al., 2025; Sun et al., 2024; Zhao et al., 2024a). Materials such as SiO₂ (Chen et al., 2025; Gong et al., 2021; Jia et al., 2021; Zhou et al., 2019), Fe₃O₄ (Lakshmeesha et al., 2018; Lv et al., 2020; Paryoto et al., 2023), Al₂O₃ (Akash et al., 2025; Taleb et al., 2021; Yu et al., 2023), and TiO₂ (Pandit et al., 2024; Wang et al., 2025) have been explored. The core

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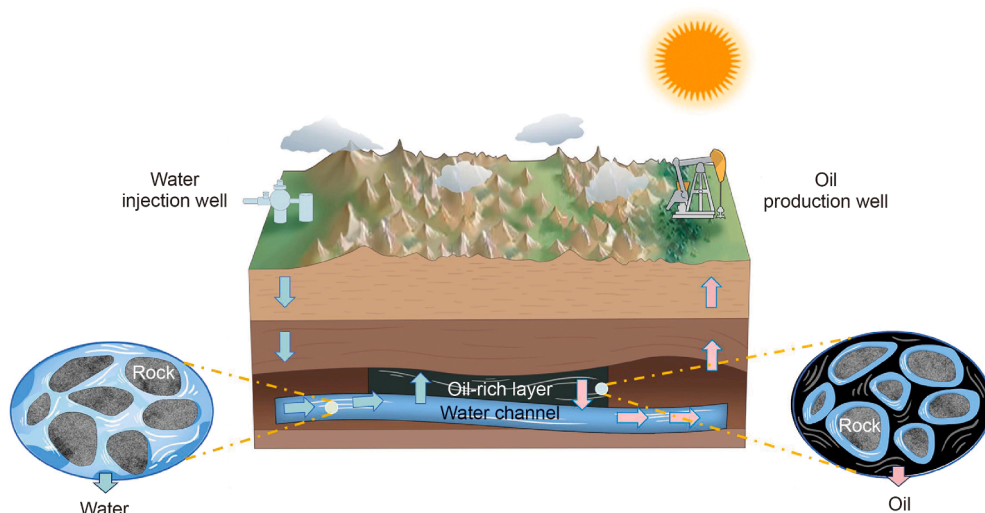


Fig. 1. Diagram of water flooding process in an oil reservoir.

principle revolves around the precise control of physicochemical properties with the goal of constructing dynamic water shutoff networks that are compatible with complex pore throat structures. Extensive research has focused on developing high-performance nanomaterials, ranging from environmentally friendly natural surfactants (Bahraminejad et al., 2021, 2022) to multifunctional nanocomposites designed to synergistically optimize interfacial tension (IFT) and wettability (Bahraminejad et al., 2019, 2024). For example, Pickering emulsions leverage nanoparticle adsorption at the oil–water interface for stabilization (Wu and Ma, 2016). Changes in the nanoparticle surface can be induced by applying external stimuli such as pH (Chen et al., 2024; Dai and Li, 2023; Liu et al., 2023; Sia et al., 2023; Yang et al., 2021), magnetic fields (Fan et al., 2024; Fu et al., 2022; Guo et al., 2024; Hu et al., 2025; Mu et al., 2024), and temperature (Li et al., 2023), allowing the surface properties to balance water shutoff efficiency while minimizing oil-phase permeability loss. However, despite these advancements, a fundamental and persistent unresolved challenge for pre-synthesized nanomaterials, whether simple nanoparticles or complex composites, is the migration–aggregation dilemma. The inherent high-temperature/high-pressure reservoir conditions and the complex brine chemistry result in the instability of nanoparticles through surface hydroxyl aggregation or electrolyte adsorption (Zhang et al., 2025), which significantly reduces the shutoff performance (Wang et al., 2024b). At present, prefabricated nanoparticle technology faces three primary challenges (Foroozesh and Kumar, 2020; Lai et al., 2022): (1) Irreversible aggregation occurs during long-distance migration due to the collapse of the DLVO potential barrier, often resulting in near-wellbore shutoff and shutoff failure. (2) The high cost of surface modification limits field applications. (3) Reservoir pore throat heterogeneity requires precise adjustment of particle size distribution for effective water shutoff (Etehad et al., 2019; Pu et al., 2023). Furthermore, the performance of such systems is highly lithology-dependent, which adds further challenges to their application in heterogeneous formations (Manshad et al., 2024).

Notably, alkoxysilanes, particularly tetraethyl orthosilicate (TEOS), present a promising alternative due to their ability to form silica nanoparticles under controlled conditions. Previous research has demonstrated that solvent composition can regulate silica particle size through hydrolysis–condensation of TEOS, yet the gelation process is often compromised by high sensitivity to temperature, which adversely affects application reliability (Bari et al., 2020; Verschraegen et al., 2023). To fundamentally resolve

the migration–aggregation dilemma and eliminate the need for precise size matching in heterogeneous formations, this study proposes a novel strategy: enabling the *in situ* formation of functional silica nanonetworks directly within reservoir pore throats. Accordingly, a novel water shutoff system based on the *in situ* hydrolysis–polymerization of a TEOS emulsion is developed for high-temperature, high-salinity reservoir environments. While this technology contributes to the broader goal of conformance control, its core function is selective water shutoff in production wells, with potential applicability in injection wells for profile modification. The emulsion template modulates reaction kinetics, harnessing reservoir conditions to facilitate nanoparticle formation. Its distinct features include: (1) Emulsion precursor injection avoids migration losses caused by aggregation of pre-synthesized nanoparticles. (2) Glycerol regulates the polarity/colloidal stability of the reaction microenvironment, enabling precise control of the *in situ* SiO₂ nanoparticle size and dispersibility, and accurately matching heterogeneous pore throat structures. (3) Nanoparticle shutoff stability is enhanced through adsorption and chemical bonding of silanol groups/surfactants on the rock surface. To elucidate the dynamic shutoff mechanism, we employed quasi-*in situ* Raman spectroscopy and complementary techniques to track silica nanoparticle formation. Rheology and core flooding experiments systematically evaluated the selective shutoff performance. Finite element simulation and atomic force microscopy (AFM) investigated nanoparticle retention mechanisms. A computational fluid dynamics–discrete element method (CFD–DEM) model was established to visualize nanoparticle migration, bridging, and shutoff behavior in porous media. Simultaneously, AFM force–distance curves quantitatively revealed the enhanced anchoring force from surfactant modification. By fundamentally addressing the efficiency limitations of conventional water-flooding, this study contributes to the broader goal of optimizing energy input and maximizing resource output in the energy industry.

2. Experimental section

2.1. Materials and emulsion preparation

2.1.1. Materials

The reagents used in this study included glycerol (99.0%), sorbitan monolaurate (Span 80, 99.0%), tetraethyl orthosilicate (TEOS, 99.0%), fatty alcohol polyoxyethylene ether (AEO, 99.0%), sodium

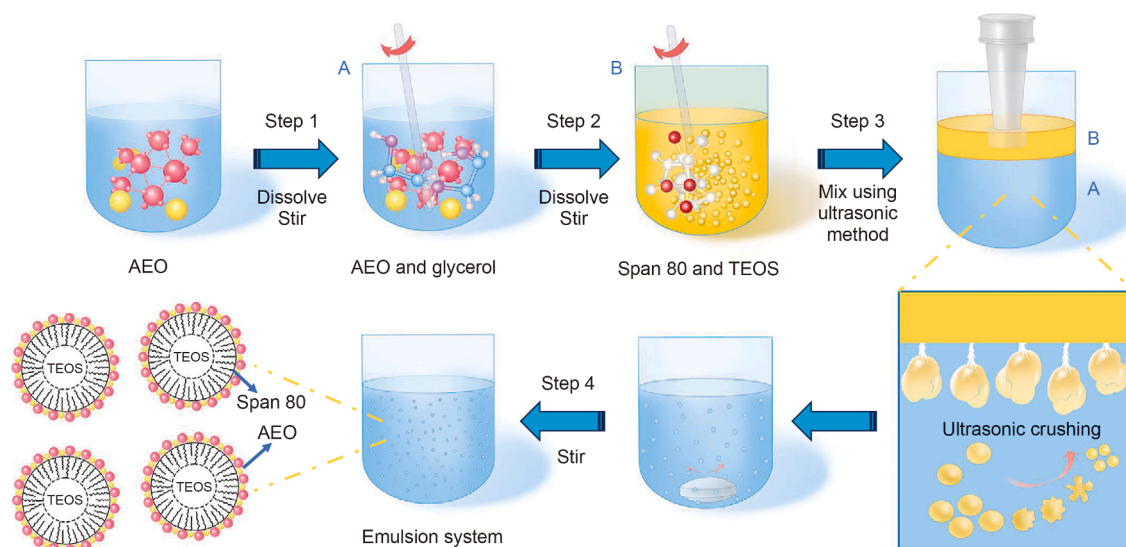


Fig. 2. Process flow diagram for emulsion system preparation.

chloride (NaCl, 99.5%), calcium chloride (CaCl_2 , 96.0%), and magnesium chloride (MgCl_2 , 96.0%). All chemicals were purchased from Chengdu Kolon Chemical Co., Ltd. (China) and used as received. The experiments were conducted using ultrapure water (resistivity $18.25 \text{ M}\Omega\cdot\text{cm}$ at 25°C), which was prepared using a water purification system (CDUPT-III, Chengdu Ultrapure Technology Co., Ltd., China). The water quality met ASTM D1193-06 Type I specifications, ensuring the experiments were conducted using water of the highest purity. The simulated formation water used in this study had a salinity of $10,000 \text{ mg/L}$ and was prepared by dissolving 7.0 g sodium chloride (NaCl), 2.0 g calcium chloride (CaCl_2), and 1.0 g magnesium chloride (MgCl_2) per liter of deionized water.

2.1.2. Emulsion preparation procedure

The formulated system comprises tetraethyl orthosilicate (TEOS), sorbitan monolaurate (Span 80), fatty alcohol polyoxyethylene ether (AEO), glycerol, and deionized water, with the preparation protocol detailed in Fig. 2(a). Glycerol was completely dissolved in deionized water. AEO was added to the glycerol solution and stirred until completely dissolved. Separately, Span 80 was dissolved in TEOS. The glycerol/AEO aqueous solution was placed in an ultrasonic homogenizer. The instrument was set to the desired power, and the ultrasonic probe was immersed. Ultrasonication was started while the Span 80 and TEOS organic phase solution was simultaneously dripped into the aqueous phase at a constant rate. This was continued until emulsification was complete and the desired emulsion system was achieved. The detailed composition, purity, and mass fraction of each chemical reagent required for emulsion preparation are summarized in Table 1.

Table 1
Composition and mass fractions of chemical reagents in the emulsion.

Composition	Purity, %	Mass fraction, wt%
H_2O	N/A	65.8
$\text{C}_3\text{H}_8\text{O}_3$	≥ 99.0	8.0
TEOS	≥ 99.0	22.0
Span 80	≥ 99.0	2.7
AEO	≥ 99.0	1.5

2.2. Emulsion stability and reaction process analysis

2.2.1. Demulsification time determination

The emulsion system was diluted 10-fold with simulated formation water (salinity of $10,000 \text{ mg/L}$) and aged in a drying oven at 100°C . It should be noted that the selection of the aforementioned temperature and salinity simulates the typical characteristics of mature oilfields in eastern China. These conditions are consistent with the actual reservoir environment targeted by this water shutoff technology. The time at which phase separation was complete was used as the aging time for subsequent core displacement experiments.

2.2.2. Dielectric constant measurement

The dielectric constants of emulsions containing different glycerol concentrations (0%, 2%, 5%, and 8%) were measured using a Novocontrol Concept 42 broadband dielectric spectrometer. The instrument was precisely calibrated with deionized water before testing. The measurement frequency range was 100 Hz to 100 kHz . The dielectric constant values reported and discussed in this study were measured at a fixed frequency of 100 kHz . This frequency was selected because it is high enough to minimize the influence of electrode polarization effects and thus reliably characterize the bulk polarity of the reaction microenvironment affected by glycerol.

2.2.3. Raman spectroscopy

The emulsion samples were first aged under simulated reservoir conditions (100°C , $10,000 \text{ mg/L}$ salinity) in a temperature-controlled oven for the specified durations (0, 2, 5, 8, and 10 h). After each aging period, the samples were promptly removed from the oven and immediately placed in an ice bath to rapidly cool them to room temperature (approximately 25°C). The Raman measurements were then performed at ambient temperature and pressure on these pre-aged samples.

2.2.4. Optical microscopy

The evolution of the emulsion system morphology was monitored using an Olympus BX53 microscope during the aging process at different times (0, 5, 10, and 12 h) under reservoir conditions.

2.2.5. IFT measurement

The emulsion system was first centrifuged at a low speed of 2500 rpm and the lower liquid layer was collected using a micro syringe for later use. The same sampling method was applied to the demulsified system (aged for 8 h) and the silica fully formed system (aged for 12 h). The IFT values of the three liquids with the ester were measured using a German Lauda Scientific LSA100 contact angle/surface tension meter.

2.3. Characterization of *in situ*-generated nanoparticles and networks

2.3.1. Zeta potential and particle size analysis

The effect of glycerol concentration on the zeta potential and particle size distribution of *in situ*-generated silica nanoparticles was determined using a Malvern Zetasizer Nano ZS90 analyzer. The test samples were prepared by diluting emulsions (containing 0, 2, 5, or 8 wt% glycerol) with simulated formation water at a ratio of 10:1 to generate silica under reservoir conditions. The storage stability of the produced silica was also evaluated by measuring the particle size and zeta potential after aging for 15 d at room temperature.

2.3.2. Scanning electron microscopy

The morphology and particle size of the *in situ*-generated silica were characterized using a field emission scanning electron microscope (FE-SEM, ZEISS Sigma 300, Germany). For sample preparation, the silica suspension obtained after aging was centrifuged at 6000 rpm for 15 min. The collected precipitate was washed three times with anhydrous ethanol to remove residual surfactants and salts, and then re-dispersed in ethanol via ultrasonication for 5 min. A drop of the well-dispersed suspension was deposited onto a clean silicon wafer and dried naturally at ambient temperature. To enhance conductivity and minimize charging effects, the dried sample was sputter-coated with a thin gold layer (Quorum SC7620, 10 mA, 45 s) prior to imaging. Observations were conducted at an accelerating voltage of 3 kV using the SE2 detector.

Furthermore, to directly visualize the plugging behavior of silica particles within the pore spaces, a core sample was collected after the displacement experiment. Following injection of the system and aging under reservoir conditions (100 °C, 10,000 mg/L salinity) for 12 h, the core was sliced into approximately 1 cm thick sections using a cutting machine. The freshly exposed surfaces of these core slices were then examined under SEM to observe the distribution and shutoff state of the *in situ*-generated silica nanonetworks within the porous matrix.

2.3.3. FT-IR analysis

The organic functional groups on the surface of SiO₂ nanoparticles were analyzed in the mid-infrared region (400–4500 cm⁻¹) using a WQF-520 Fourier transform infrared spectrometer to confirm the adsorption of surfactants onto the nanoparticles.

2.4. Dynamic rheology measurement

Multiscale rheological analysis of the emulsion system diluted with simulated formation water was conducted using a Waters DHR-2 rotary rheometer. All rheological tests were performed on the fresh, non-demulsified emulsion system. A Peltier-controlled plate with an active thermal hood was used; the sample was heated to target temperatures via a programmed ramp and equilibrated for ≥300 s, maintaining temperature at the measuring gap. First, the viscosity of the emulsion system was measured at a simulated formation shear rate (100 s⁻¹) within the

temperature range of 25 to 100 °C to quantify its injectivity. Then, the storage modulus (G') and loss modulus (G'') were measured at 1% strain and 1 Hz frequency within the same temperature range using dynamic oscillation mode to assess the structural stability of the emulsion system. A three-segment thixotropic ring test (shear rate sequence: 0.1–1000–0.1 s⁻¹) was further used to quantitatively characterize the shear resistance of the emulsion system. Finally, the response characteristics of G' and G'' were measured at a fixed frequency of 1 Hz and over a wide strain range of 0.01%–1000% based on the reservoir strain range, revealing the system's adaptability to complex reservoirs.

2.5. Displacement experiments and shutoff mechanism investigation

2.5.1. Sand-filled tube displacement test

Fig. 3 shows a schematic diagram of the displacement process used in this study. The shutoff performance test used a 2.5 cm × 30 cm sand-filled tube with a permeability range of 100 to 2000 mD. After saturating the sand-filled tube with simulated formation water, a three-stage flooding experiment was conducted: emulsion flooding, emulsion aging, and water flooding. The pressure at each stage was recorded, and the permeability was calculated using Darcy's equation to reflect the system's shutoff performance at different permeabilities. Based on the water shutoff performance test, three groups of permeabilities were selected within the range of 100 to 1000 mD to evaluate the shutoff performance of the emulsion system. In the oil-phase shutoff performance test, after saturation of the sand-filled tube with simulated formation water, five displacement experiments were carried out in sequence: simulated formation water flooding, oil flooding, emulsion flooding, emulsion aging, and oil flooding. The pressure was recorded at each stage, and the permeability was calculated using Darcy's law to evaluate the oil-phase shutoff performance of the emulsion system. For each permeability level, three parallel replicate experiments were conducted.

Darcy's law is given by Eq. (1):

$$K = \frac{q\mu L}{A\Delta P} \quad (1)$$

where K is the permeability, mD; q is the injection rate, mL·min⁻¹; μ is the fluid viscosity, mPa·s; L is the core length, cm; A is the cross-sectional area, cm²; and ΔP is the pressure drop, MPa.

Residual resistance factor (F_{rr}) was calculated as follows:

$$F_{rr} = \frac{K_1}{K_2} \quad (2)$$

where K_1 is the initial permeability, mD; and K_2 is the post-treatment permeability, mD.

Shutoff efficiency (η) was calculated using the following expression:

$$\eta = \frac{K_1 - K_2}{K_1} \times 100\% \quad (3)$$

2.5.2. Contact angle and wettability analysis

The static/dynamic contact angle was measured using a WAM-80 automatic contact angle meter on the silica generated *in situ*. To obtain the test sample, the emulsion system was first aged under simulated reservoir conditions (100 °C, 10,000 mg/L salinity) for 12 h to allow for demulsification and silica formation. The

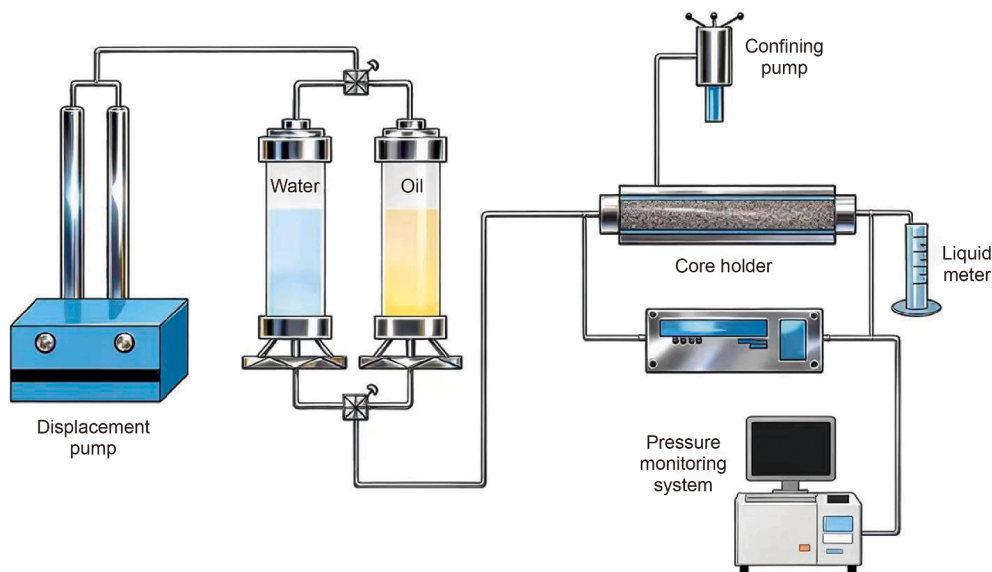


Fig. 3. Schematic diagram of the displacement process.

resulting silica was then collected, cooled to ambient temperature (25 °C), and prepared for measurement.

2.5.3. X-ray photoelectron spectroscopy

XPS samples (quartz sand) were taken from sand-pack displacement experiments after aging at 100 °C for 12 h. The samples were rinsed with deionized water to remove free ions and then dried in a vacuum oven at 60 °C for 24 h before being transferred to the XPS instrument. XPS measurement itself was performed at room temperature under ultra-high vacuum, and the obtained surface elemental and chemical-state information reflects the firmly adsorbed surface composition after high-temperature aging treatment.

2.5.4. Atomic force microscopy

This study characterized both the fresh emulsion and the emulsion aged for 10 h under simulated reservoir conditions via force–distance curve measurements and morphological characterization using a Bruker Dimension Icon atomic force microscope. AFM measurements were conducted at room temperature and ambient atmosphere on samples that had undergone the aging treatment. After probe calibration against a blank substrate, the substrate was immersed in the test emulsion for 5 min, and force–distance curves were acquired to quantify adhesion forces. Morphological characterization was then performed.

2.5.5. Finite element modeling

A computational fluid dynamics–discrete element method (CFD–DEM) was established to reveal the migration and shutoff mechanism of SiO₂ nanoparticles in porous media (Yang et al., 2020). Firstly, a porous medium model with representative pore-throat structures was generated on the EDEM platform using a random particle stacking approach. Secondly, the dynamic generation of SiO₂ nanoparticles in the pore flow field was realized in Fluent. Finally, the migration trajectory and shutoff behavior of particles in the porous medium were analyzed visually through coupled simulation. Additional simulation results, including the baseline flow fields without particles, are presented in Supplementary Material (Figs. S6–S10). The simulation parameters and numerical setup are provided in detail in Section S7 in Supplementary Material. Additionally, the primary objective of the

simulation was to achieve qualitative visualization and mechanistic understanding of particle migration and plugging, rather than the quantitative prediction of absolute shutoff efficiency for individual cores.

3. Results and discussion

3.1. The formation process of SiO₂

Understanding the controlled formation of silica nanoparticles from the TEOS emulsion under reservoir conditions is fundamental to the shutoff process. Raman spectroscopy analysis (Fig. 4(a)) reveals distinct reaction stages. During the initial aging stage (0–8 h), no characteristic siloxane backbone signals were observed, and the peak intensity of the Si–O–C bond in TEOS (660 cm^{−1}) remained stable (Schmitt, 2014). At the same time, the peak intensity of the C–O–C bond (1000–1200 cm^{−1}) gradually decreased (Bhatta et al., 2022), suggesting a period dominated by the reorganization of the Span 80/AEO surfactant mixture at the emulsion interface, with minimal TEOS hydrolysis occurring. During the subsequent aging stage (>9 h), the Si–O–Si peak emerged and significantly enhanced, while the Si–O–C and C–O–C bonds decayed. This suggests that the accumulated surfactant reorganization ultimately triggers the hydrolysis and condensation of TEOS, accelerating the formation of the Si–O–Si framework.

To quantitatively characterize this reaction process, the temporal evolution of the normalized Si–O–Si peak intensity was analyzed. Considering the complex, emulsion-triggered reaction environment, the formation of the silica network under reservoir conditions was modeled as an apparent first-order process following demulsification. The experimental data were fitted using the following equation:

$$I_{\text{Si-O-Si}}(t) = I_{\text{max}}(1 - e^{-kt}) \quad (4)$$

where $I_{\text{Si-O-Si}}(t)$ is the normalized peak intensity of the Si–O–Si bond at reaction time t ; I_{max} is the normalized peak intensity of the Si–O–Si bond at complete reaction; and k is the apparent rate constant. The experimental data under simulated reservoir conditions (100 °C, 10,000 mg/L salinity) were fitted by the nonlinear

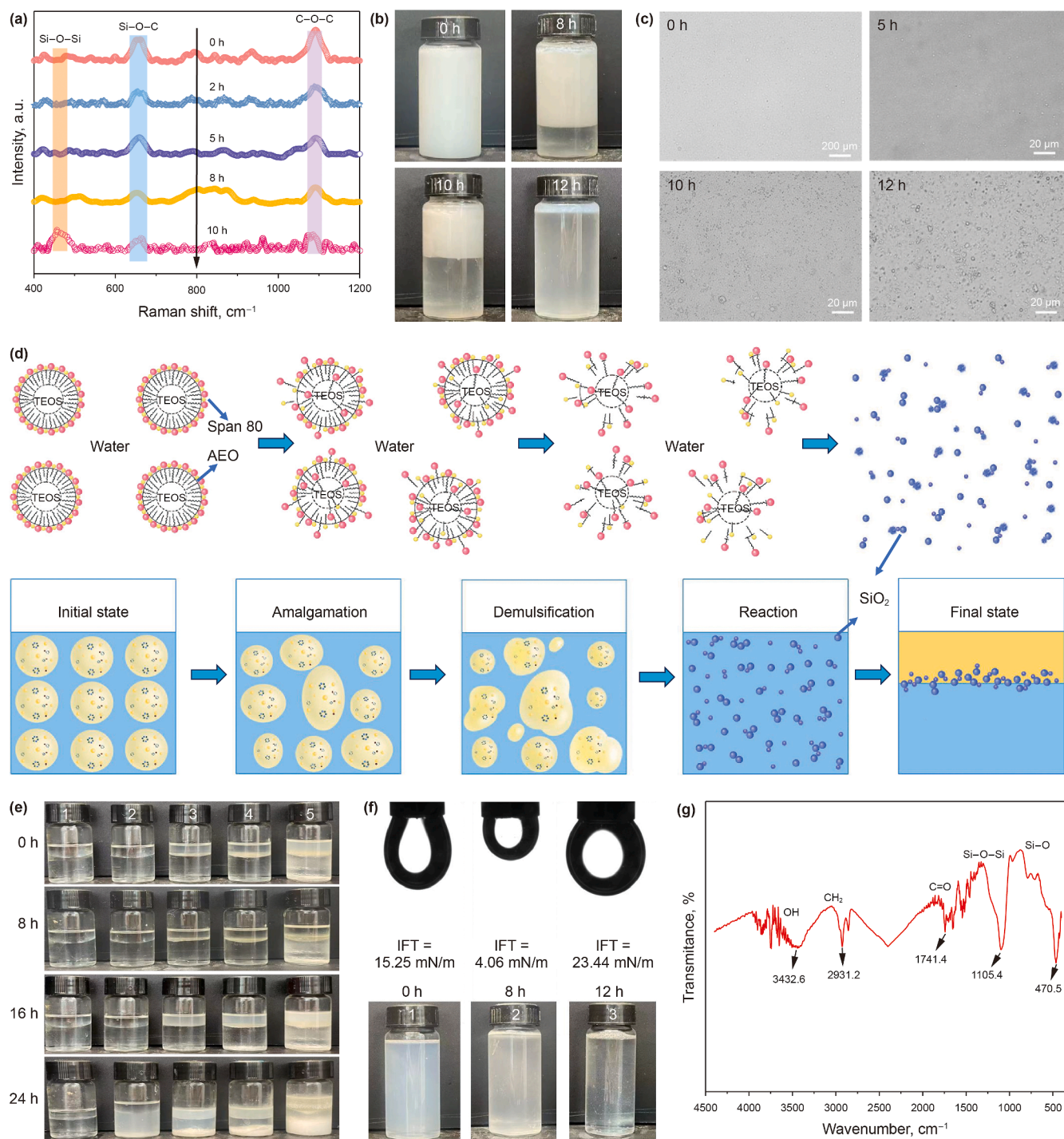


Fig. 4. (a) Raman spectra of the system at different aging times; (b) changes of the emulsion system over time in a simulated reservoir environment; (c) optical microscopic images of the emulsion at different aging times; (d) schematic illustration of the dynamic evolution from demulsification to *in situ* generation of SiO_2 nanoparticles (react denotes the hydrolysis–condensation of TEOS involving TEOS, H_2O , and released surfactants); (e) effect of surfactant concentration on silica generation time; (f) IFT changes during the reaction process; (g) FT-IR spectrum of *in situ*-generated SiO_2 nanoparticles.

least squares method, yielding an apparent rate constant $k = 0.29 \pm 0.03 \text{ h}^{-1}$ with a goodness of fit $R^2 > 0.98$. The detailed quantitative kinetic analysis using Raman spectroscopy data is provided in Section S1 in Supplementary Material. This indicates that the apparent first-order reaction model can well describe the reaction process. Based on the kinetic parameters, the reaction half-life of silica network formation was further calculated as $t_{1/2} = \ln(2)/k \approx 2.4 \text{ h}$. This quantitatively derived half-life is in

excellent agreement with the experimental observation that visible silica particles began to form at approximately 3 h in the system containing 3.3 wt% surfactant (Table 2). This congruence provides direct kinetic validation for the core mechanism, confirming that demulsification triggers the rapid and synchronous hydrolysis and condensation of TEOS, and that the reaction rate is well-suited to the time requirements for field application in reservoirs.

Table 2

Experimental system composition and the effect of surfactant concentration on silica formation time.

Number	Deionized water, wt%	Simulated formation water, wt%	TEOS, wt%	Surfactant, wt%	Particle formation time, h
1	75	0	25	0	>24
2	0	75	25	0	>24
3	0	75	25	3.3	3
4	0	75	25	6.6	2
5	0	75	25	9.9	1

The thermal stability test results and optical microscopy observations of emulsions aged for different times are shown in Fig. 4(b) and (c). The macroscopic phase separation and emulsion collapse occurred after 8 h of aging (Fig. 4(b)). And the droplet size increased significantly with increasing aging time (Fig. 4(c)), indicating that the emulsion was undergoing demulsification and aggregation. Irregular silica aggregates formed after aging for 10 h. Fig. 4(d) further depicts the process of emulsion demulsification and subsequent formation of silica nanoparticles. Emulsion droplet aggregation and collapse are prerequisites for TEOS heterogeneous nucleation.

Fig. 4(e) and Table 2 reveal the influence of surfactant concentration on particle formation time under reservoir conditions. It is worth noting that no silica particles formed in the surfactant-free system within 24 h. However, with the addition of just 3.3 wt% surfactant, the particle formation time sharply dropped to 3 h. As the surfactant concentration continued to rise to 6.6 and 9.9 wt%, the particle formation rate accelerated, taking just 2 and 1 h, respectively. These data provide powerful proof that surfactants act as a strong nucleation promoter in the TEOS hydrolysis–condensation reaction. The thermodynamic driving mechanism of this phenomenon can be analyzed using classical nucleation theory. The nucleation barrier (ΔG^*) is expressed as follows (Lutsko, 2018):

$$\Delta G^* = \frac{16\pi\gamma^3}{3(\Delta G_v)^2} \quad (5)$$

where ΔG_v represents the change in volumetric free energy; and γ is the interfacial energy.

Eq. (5) shows that a decrease in γ significantly reduces ΔG^* , thereby promoting nucleation. In this surfactant-dominated system, the sharp reduction in IFT serves as a practical and indicative proxy for the decrease in solid–liquid interfacial energy (γ) within the framework of classical nucleation theory. This approach is justified because that (1) the release and adsorption of surfactants lower both the liquid–liquid and nascent solid–liquid interfacial energies; and (2) the observed strong correlation between IFT reduction and nucleation acceleration supports its use as a key influencing factor. We note that directly equating IFT to γ is an approximation, as the solid–liquid γ is also influenced by factors such as surface structure. However, for the purpose of elucidating the surfactant-mediated nucleation trend, the IFT provides a valid and measurable indicator of the changing interfacial energetics. In accordance with the literature (Cassar, 2019), the IFT and interfacial energy are numerically equal. The release of surfactant during emulsion phase separation caused the IFT of the lower liquid to drop rapidly from 15.25 to 4.06 mN/m (Fig. 4(f)). This decrease significantly reduced the nucleation barrier, thereby accelerating the nucleation of silica. Notably, the IFT recovered sharply to 23.44 mN/m after the formation of silica. FT-IR analysis (Fig. 4(g)) confirmed the presence of C=O (1741 cm^{-1}) and CH₂ (2931 cm^{-1}) groups on the particle surfaces (Wang et al., 2021), proving that surfactants were adsorbed onto their surfaces, thereby reducing the surfactant content in the lower liquid and increasing the IFT.

This reveals a dual role of the surfactant. Upon demulsification, the release of the surfactant promotes nucleation by drastically reducing the IFT and energy barrier; subsequently, the surfactant adsorbs onto the newly formed silica nanoparticles, altering the surface wettability, which lays the foundation for selective shutoff.

3.2. Regulation of silica particle size

Precise control over the size of *in situ*-generated SiO₂ nanoparticles is crucial for effectively blocking the multi-scale pore throats in heterogeneous reservoirs. SEM images (Fig. 5(a)) revealed that increasing glycerol concentration from 0 to 8 wt% increased the primary particle size from 54.02 to 120.46 nm and intensified aggregation. To quantitatively elucidate the mechanism of this glycerol-mediated aggregation, we systematically characterized the changes in the reaction microenvironment and the resultant colloidal properties. First, the substantial decrease in the dielectric constant (ϵ) from 226.24 to 78.65 (Fig. 5(b)) confirmed that glycerol reduced the polarity of the reaction microenvironment through its dense hydrogen-bond network with water molecules. This altered polarity fundamentally affects the hydrolysis–condensation kinetics of TEOS, promoting the growth of larger primary particles. The relationship between dielectric constant (ϵ) and the mean hydrodynamic diameter of aggregates (d) was best described by an exponential decay model ($d =$

$2163.5 - 672.09e^{-\frac{(\epsilon - 226.24)^2}{47.23}}$, $R^2 = 0.68$), indicating that once the dielectric constant falls below a certain threshold, its promoting effect on particle growth gradually weakens. To further reveal the physical meaning of the fitting parameters in this exponential model and the intrinsic limit of glycerol's regulatory effect, we conducted an in-depth analysis of the correlation between the model's core parameters and experimental observations. The plateau value of hydrodynamic diameter (2163.5 nm) in the model represents the upper limit of silica aggregate size achievable by glycerol-mediated dielectric tuning under the experimental conditions, and the emergence of this plateau effect stems from the critical state of system polarity when the dielectric constant of the reaction microenvironment drops to approximately 78.65 (corresponding to 8 wt% glycerol). At this point, the solvation effect and electrostatic repulsion of silica precursors are weakened to a nearly constant level, and the driving force for TEOS hydrolysis–condensation and subsequent particle aggregation can no longer be enhanced by further reducing the dielectric constant, ultimately leading to the saturation of particle size growth. The decay coefficient (47.23) in the model directly reflects the sensitivity of silica aggregate size to the variation of microenvironmental polarity. This value in our experimental system indicates that the particle size is highly sensitive to changes in dielectric constant within the range of 185.94–226.24 (corresponding to 0–5 wt% glycerol), while this sensitivity decreases sharply when the dielectric constant is lower than 185.94, which is highly consistent with the experimental observation that the particle size growth rate slows significantly when the glycerol concentration is increased to 8 wt%. Meanwhile, the model takes 226.24 as the

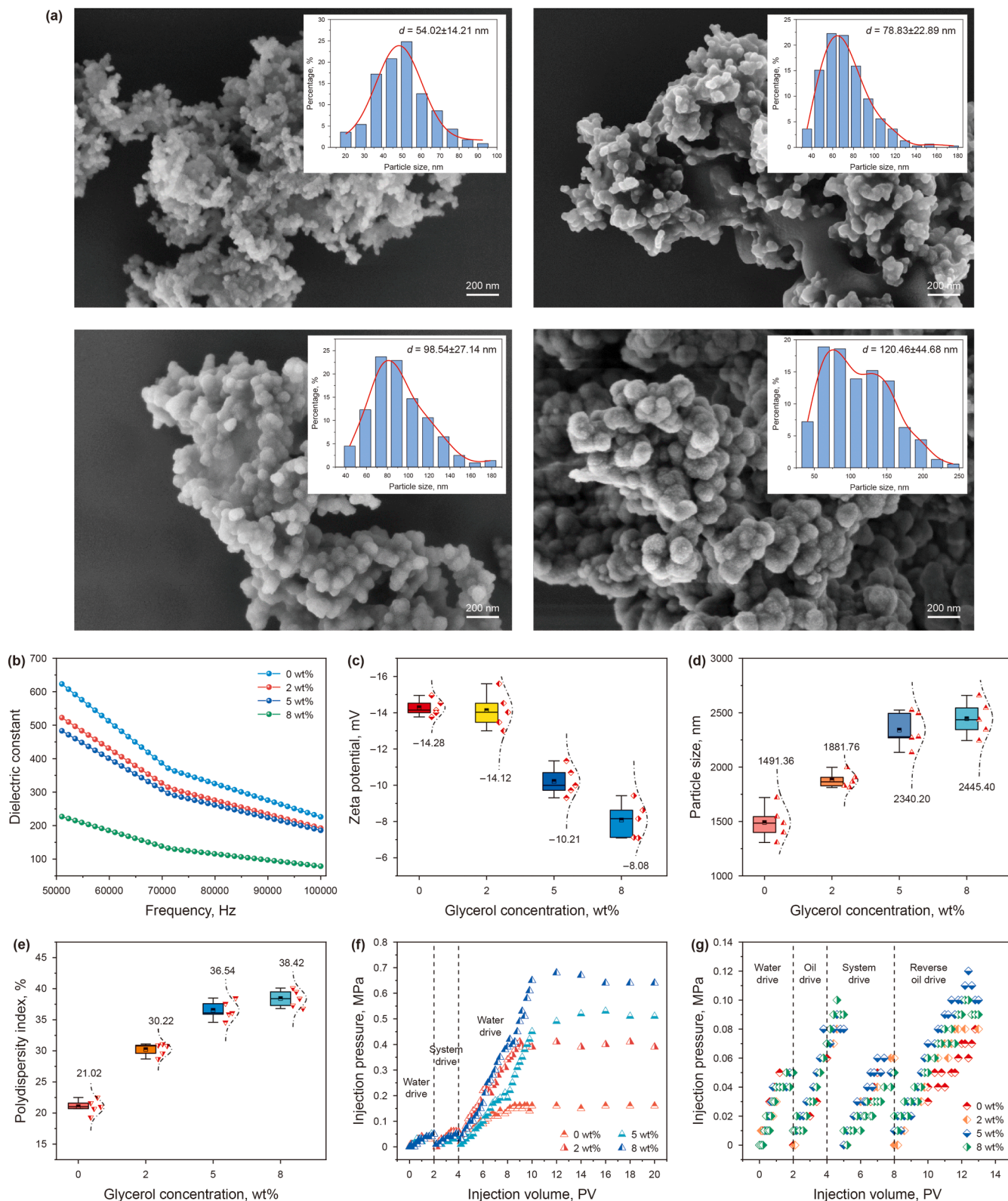


Fig. 5. (a) SEM images showing the morphology and primary particle size of SiO₂ nanoparticles (simulated reservoir conditions: 100 °C, 10,000 mg/L salinity) synthesized at different glycerol concentrations; (b) effect of glycerol concentration on the dielectric constant (measured at 100 kHz) of emulsion systems; (c) effect of glycerol concentration on the zeta potential of silica nanoparticles; (d) effect of glycerol concentration on the particle size of silica nanoparticles; (e) effect of glycerol concentration on the polydispersity index of silica nanoparticles; (f, g) effect of glycerol concentration on shutoff performance.

Table 3

Effect of glycerol concentration on dielectric properties and shutoff performance of the emulsion system.

Number	Glycerol concentration, wt%	Dielectric constant measured at 100 kHz	Zeta potential, mV	Permeability, mD	Water shutoff efficiency, %	Oil shutoff efficiency, %
1	0	226.24	−14.28	208.50	68.72	18.24
2	2	192.60	−14.12	208.50	87.19	19.88
3	5	185.94	−10.21	208.50	90.22	27.28
4	8	78.65	−8.08	208.50	92.18	25.05

initial dielectric constant reference point, corresponding to the maximum polarity state of the reaction microenvironment without glycerol addition, where the silica aggregate size is at the minimum value (1491.4 nm) in the experiment due to the strongest solvation effect and electrostatic repulsion of the system.

This trend aligns with our proposed physical mechanism. Glycerol reduces polarity, thereby weakening the solvation effect and electrostatic repulsion of silica precursors, which accelerates particle growth and aggregation. When the polarity drops to a lower level, other factors may become dominant, causing the size increase to gradually plateau (detailed calculations are provided in Section S2 in Supplementary Material). Together, the quantitative decrease in dielectric constant and the exponential response model for aggregate size provide consistent thermodynamic and kinetic evidence that glycerol, by tuning microenvironment polarity, serves as a key factor enabling controllable size-directed aggregation of silica nanoparticles.

Second, the lower polarity fundamentally altered the hydrolysis–condensation kinetics of TEOS, promoting the formation and growth of larger primary particles. Simultaneously, the reduced-polarity microenvironment destabilized the colloidal system. Zeta potential analysis confirmed this destabilization, showing a decrease in the absolute value $|\zeta|$ from 14.28 to 8.08 mV (Fig. 5(c)), which indicates a lowered surface charge density and weakened electrostatic repulsion between particles. Consequently, dynamic light scattering (DLS) measurements with five independent replicates per condition ($n = 5$) showed that the mean hydrodynamic diameter of the aggregates increased systematically from 1491.4 ± 145.9 to 2245.2 ± 158.4 nm (Fig. 5(d)), accompanied by a broadening of the polydispersity index (PDI) from 21.02% to 38.42% (Fig. 5(e)). This glycerol-tunable aggregation state directly translated into enhanced plugging performance. As shown in Fig. 5(f) and (g) and Table 3, the systematic increase in aggregate size and distribution breadth resulted in a remarkable rise in water shutoff efficiency from 68.72% to 92.18%, while the oil shutoff rate remained consistently low (18.24% to 25.05%).

Therefore, glycerol-mediated regulation enables coordinated control over both the primary particle size and their subsequent aggregation state. It is critical to emphasize that the hydrodynamic diameter measured by DLS reflects the size of the functional aggregates responsible for shutoff. This synergistic control provides a key mechanistic insight: Larger and more polydisperse aggregates can effectively block a wider range of pore throats, while the concurrently increased primary particle size reinforces the mechanical stability of the resulting plugging network—thereby effectively addressing the multi-scale heterogeneity of reservoir pore structures.

3.3. Performance of emulsion systems

Having established the ability to precisely control the size and aggregation state of the *in situ*-generated nanoparticles, we next evaluated the overall performance of the emulsion system, including its stability, injectivity, and, most critically, its selective water shutoff capability. Fig. 6 systematically presents the room-

temperature stability, rheology, and selective shutoff performance of the emulsion system. Nanoparticle analysis (Fig. 6(a)–(c)) revealed an initial hydrodynamic diameter of 115 nm and a zeta potential of −55.9 mV. After 15 d of storage at room temperature, the particle size showed minimal change (118 nm) and the zeta potential remained at −54.5 mV ($\Delta\zeta < 2$ mV), demonstrating excellent colloidal stability. To further validate the long-term durability of the *in situ*-generated silica under more stringent conditions relevant to harsh reservoirs, accelerated aging tests were conducted at 130 °C and 35,000 mg/L salinity. As shown in Fig. S3, the silica maintained its morphology over 30 d without observable aggregation, fragmentation, or structural deterioration—only mild gravity-induced sedimentation occurred, which does not impair its plugging performance. The long-term state stability of silica under harsh conditions is provided in Section S5 in Supplementary Material. After aging, the dried silica exhibited a water contact angle of 129° (Fig. S4), confirming that its hydrophobicity was preserved. The surface hydrophobicity characterization of aged silica is provided in Section S6 in Supplementary Material. This retained hydrophobicity minimizes interactions with high-salinity water, thereby mitigating water-induced erosion or dissolution and ensuring long-term functional stability under extreme environments.

Steady-state shear tests (Fig. 6(d)) demonstrated temperature-dependent viscosity reduction from 1.43 mPa·s at 25 °C to 0.954 mPa·s at 100 °C, maintaining ultra-low viscosity (<1.5 mPa·s) and weak thermal sensitivity, ensuring injectability at reservoir temperatures. Small-amplitude oscillatory shear ($\gamma = 1\%$, $f = 1$ Hz; Fig. 6(e)) showed that the storage modulus (G') was greater than the loss modulus (G'') in the range of 25–100 °C, indicating elastic-dominated behavior and robust internal network formation. Despite the system's low bulk viscosity, the consistent dominance of G' over G'' indicates an elastic microstructure. This elastic component in the low-viscosity emulsion is attributed to the viscoelastic surfactant-stabilized interface and possible transient droplet–droplet interactions, contributing to emulsion stability during placement. Shear rate cycling test (0.1 – 1000 – 0.1 s^{−1}; Fig. 6(f)) confirmed structural recovery with negligible hysteresis, while strain amplitude sweeps test (Fig. 6(g)) verified that G' was always greater than G'' within the reservoir strain range ($\gamma = 0.1\%$ – 10%), ensuring structural stability under dynamic conditions.

Sand-filled tube displacement tests were conducted to quantitatively evaluate the water shutoff efficiency and oil–water selective shutoff performance of the developed system. For each permeability level (both in water shutoff and oil shutoff experiments), 3 parallel replicate experiments were performed under consistent conditions, with the first details shown in Fig. 6(h) and (i) and Tables 4 and 5. The results of the remaining two experiments and the error analysis are presented in Section S3 in Supplementary Material. Across the permeability range of 100–2000 mD, the injection pressure matched the formation-water-saturation reference pressure (Fig. 6(h) and Table 4), confirming excellent injectability. Notably, within 100–1000 mD, the water shutoff rate consistently exceeded 90% (peaking at 97.5%),

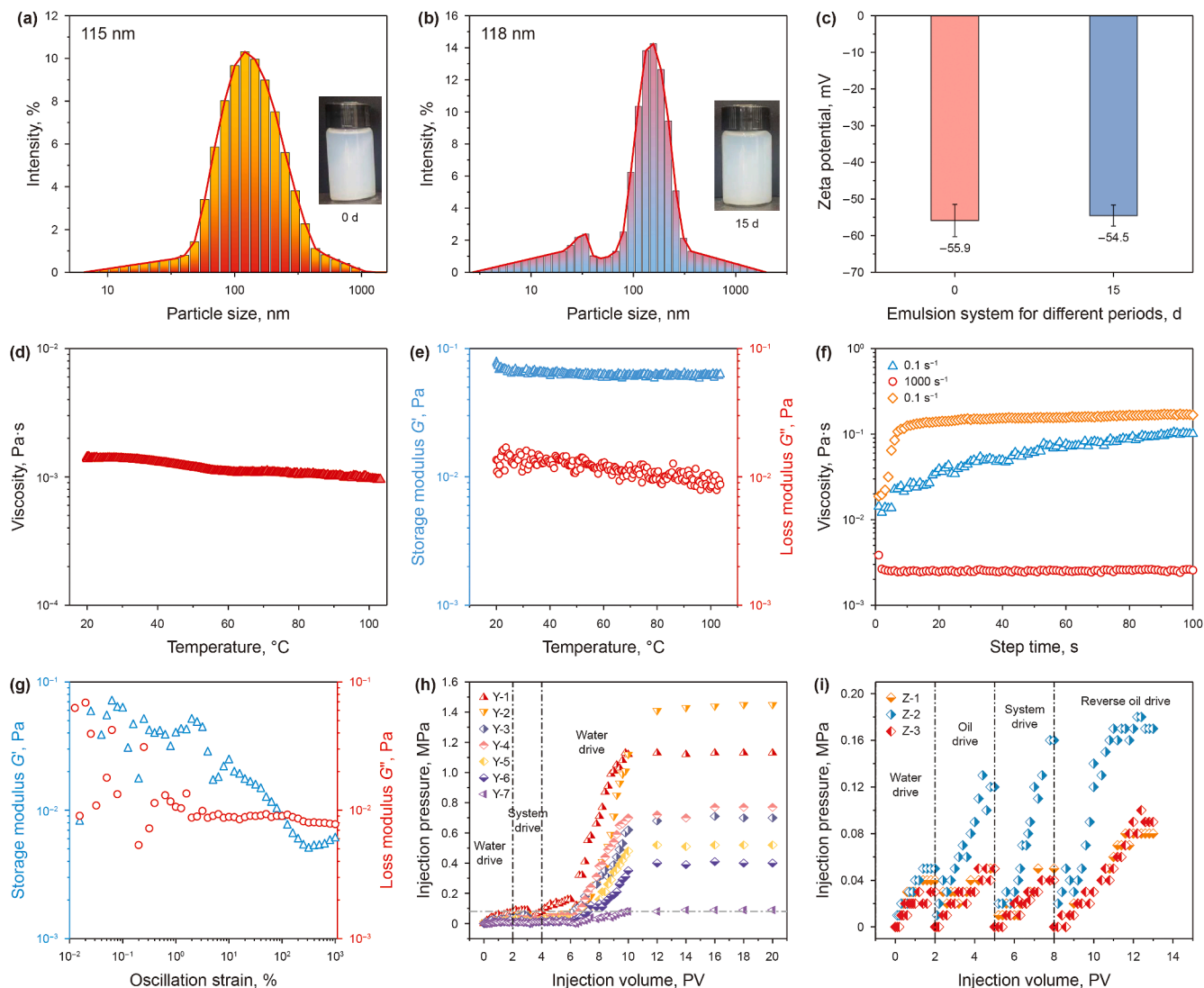


Fig. 6. (a–c) Particle size distribution and zeta potential of emulsion systems at different standing times (room temperature storage); (d–g) rheological properties of emulsions; (h, i) water drive and oil drive displacement efficiency curves.

Table 4

Water shutoff performance of sand-filled tubes with different permeabilities.

Number	Displacement rate, mL/min	Permeability, mD		Saturated water pressure, MPa	System injection pressure, MPa	Residual resistance factor F_{rr}	Water shutoff efficiency, %
		K_1	K_2				
Y-1	1	115.8	10.9	0.090	0.160	10.6	90.6
Y-2	1	173.8	7.1	0.060	0.070	24.5	95.9
Y-3	1	208.5	14.7	0.050	0.050	14.2	92.9
Y-4	1	347.5	13.5	0.030	0.040	25.7	96.1
Y-5	1	521.3	19.8	0.020	0.030	26.3	96.2
Y-6	1	1042.5	26.0	0.010	0.010	40.1	97.5
Y-7	1	2085.0	1150.0	0.005	0.005	1.8	44.8

Table 5

Oil shutoff performance of sand-filled tubes with different permeabilities.

Number	Displacement rate, mL/min	Oil permeability, mD		Saturated oil pressure, MPa	Residual resistance factor F_{rr}	Oil shutoff efficiency, %
		K_1	K_2			
Z-1	1	1096.3	851.2	0.040	1.3	22.3
Z-2	1	877.6	690.5	0.050	1.3	21.3
Z-3	1	365.1	258.4	0.120	1.4	29.2

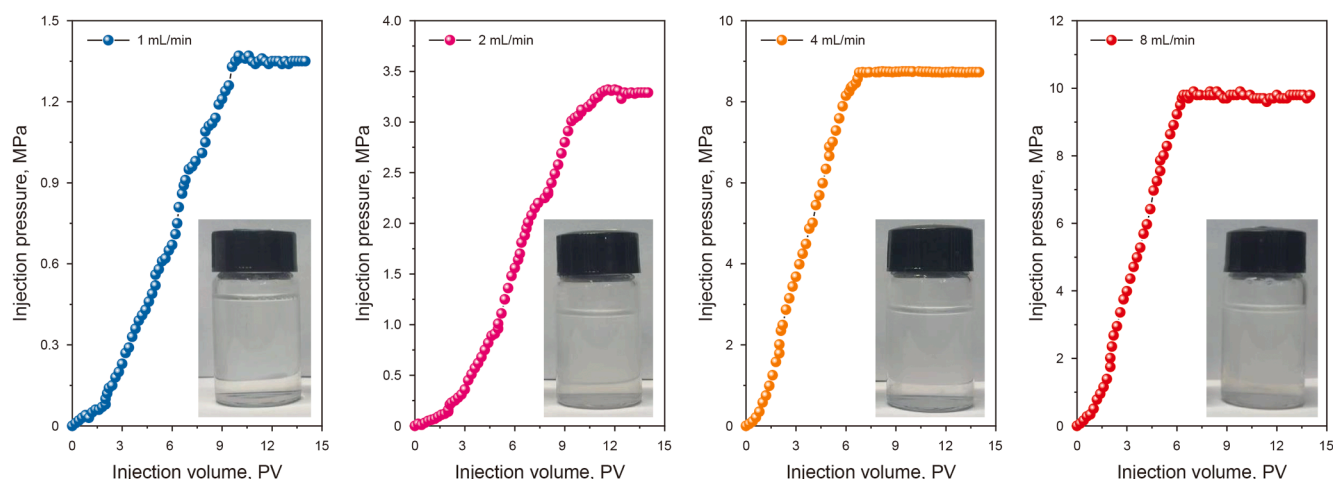


Fig. 7. Variation curves of plugging pressure under different displacement rates.

demonstrating robust size compatibility and shutoff strength for medium pore throats. The aqueous-phase residual resistance factor (F_{rr}) reached very high values (>10) in this permeability range, peaking at 40.1 at 1042.5 mD, corresponding to a 40-fold increase in water flow resistance and confirming the effective barrier formed by the *in situ*-generated nanoparticles. In contrast, at 2085 mD, the shutoff efficiency sharply declined to 44.8% due to nanoparticle packing limitations in ultra-large throats (Babakhani et al., 2017). The system also exhibited significantly weak shutoff characteristics toward the oil phase (Fig. 6(i) and Table 5). During oil-phase displacement in sand-filled tubes with permeabilities ranging from 300 to 1100 mD, the oil shutoff rate remained below 30% (minimum 21.3%), supported by consistently low oil-phase residual resistance factors (1.3–1.4), verifying minimal impact on oil flow. This marked contrast in F_{rr} values underscores the system's excellent selectivity. Critically, the effective barrier indicated by the high F_{rr} values is attributed to the exceptional stability of the *in situ*-generated silica aggregates under hydrodynamic conditions. During extended post-flush water injection (up to 15 pore volumes at rates of 1–8 mL/min), the stabilized pressure and clear effluent without visible particle loss confirm that the aggregates withstand flushing, thereby maintaining the durable shutoff of the aqueous phase while preserving oil-phase permeability (Fig. 7).

3.4. Shutoff mechanism of silica nanoparticles in reservoir pores

To further investigate the effect of surface wetting behavior of silica nanoparticles on selective water shutoff, dynamic contact angle characterization was performed. When the aqueous phase interacted with silica nanoparticles (Fig. 8(a)), the droplets maintained an approximately spherical shape throughout the approach, contact, and position adjustment process. The advancing contact angle (133.58°) and receding contact angle (147.98°) were both significantly greater than 90° , with a contact angle hysteresis (CAH) of 14.4° . This indicates weak interaction between the aqueous phase and the silica nanoparticle surface, preventing adhesive spreading and effective penetration into pore throats, thus causing water to flow around rather than through the pore network. In contrast, when the oil phase (*n*-heptane) interacted with silica nanoparticles (Fig. 8(b)), droplets rapidly spread from a spherical to a flattened shape upon contact. The low advancing (26.61°) and receding (23.27°) contact angles, with a CAH of only 3.34° , reflect strong interaction and spontaneous wetting, enabling the oil phase to spread and penetrate pore walls efficiently, thereby maintaining high oil permeability. The relatively low CAH

values for both fluids indicate uniform surfactant modification on the silica surface, which prevents local wettability fluctuations and ensures stable shutoff performance during dynamic flow.

To quantitatively link these wettability measurements to interfacial energetics and macroscopic performance, we calculated the solid–liquid adhesion work (W_{SL}) using the Young–Dupré equation. The detailed quantitative calculation using the Young–Dupré equation is provided in Section S4 in Supplementary Material. The key parameters and calculation results are summarized in Table 6. The low W_{SL} value for water (16.3 mN/m) confirms weak interaction and ineffective wetting of the hydrophobic silica surface, leading to high flow resistance and effective water shutoff. Conversely, the high W_{SL} for oil (38.3 mN/m) indicates strong interaction and spontaneous wetting, facilitating oil flow with minimal permeability reduction (detailed calculations are provided in Section S4 in Supplementary Material). This quantitative analysis directly explains the observed water shutoff efficiency of over 90% and retained oil-phase permeability of more than 70%.

As shown in Fig. 8(c), the pronounced hydrophobicity of the silica surface is further demonstrated. Water droplets placed on filter paper coated with aged silica particles maintain a spherical shape, while oil droplets spread readily. This visual evidence corroborates the contact angle and adhesion work data.

Considering factors such as preparation procedure, organic solvent content, water shutoff efficiency, oil shutoff efficiency, and injection pressure, the results of this study have comprehensive advantages over recent literature reports (Li et al., 2023; Wang et al., 2024a; Xing et al., 2025; Zhao et al., 2024b) (Fig. 8(d)), providing strong support for the application of this technology in oilfield water control.

XPS analysis was used to characterize the changes in the surface chemical composition of the quartz sand before and after sand-filled tube displacement experiments, as shown in Fig. 9(a). The evolution of carbon-containing functional groups was quantified by fitting of the C 1s peak (Liu et al., 2021). Before displacement, the atomic percentages were 27.37% for C=O, 29.52% for C–O, and 43.11% for C–C. After displacement, the C–C percentage significantly increased to 58.06%, while the C=O and C–O percentages decreased to 15.86% and 26.08%, respectively. Given that both Span 80 and AEO surfactants contain long carbon chains, this pronounced increase in C–C percentage directly indicates that the surfactant carbon chains have been successfully adsorbed onto the quartz sand surface. The decreases in the percentages of C=O and C–O are due to the adsorbed carbon chains

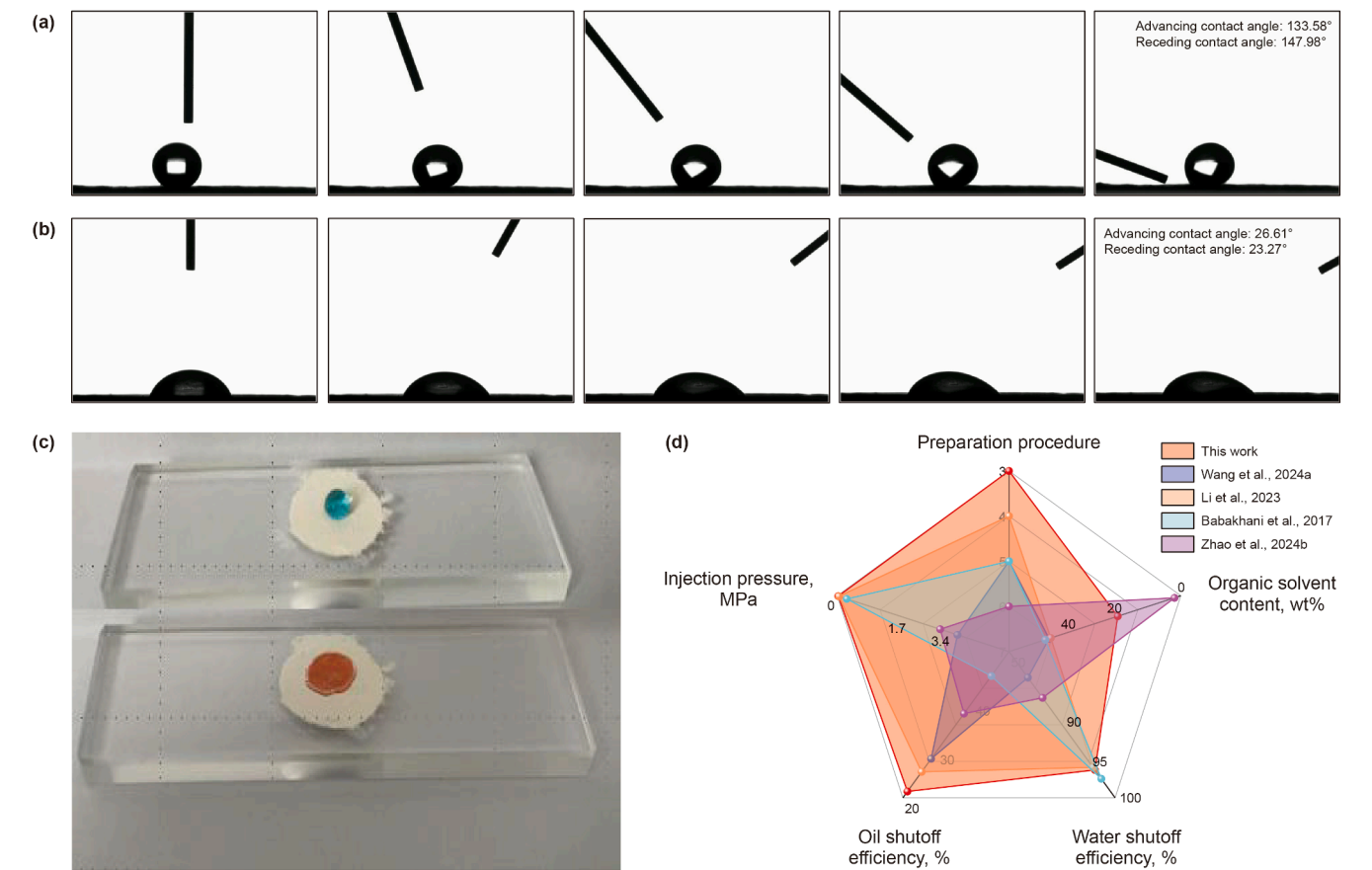


Fig. 8. (a, b) Dynamic contact angle characterization of water and oil on silica surfaces; (c) wettability of water and oil on silica surfaces; (d) comparison of comprehensive performance with related studies.

Table 6
Contact angle and calculated adhesion work for water and oil on surfactant-modified silica surfaces.

Liquid phase	Advancing contact angle, °	Receding contact angle, °	Average contact angle, °	Adhesion work W_{SL} , mN/m
Water	133.58	147.98	140.78	16.3
Oil	26.61	23.27	24.94	38.3

masking the original oxygen-containing functional groups on the quartz sand, such as surface hydroxyl groups. This surfactant adsorption behavior is closely related to the shutoff performance of silica nanoparticles, because it directly regulates the interaction between nanoparticles and the rock surface during the shutoff process, allowing the nanoparticles to be firmly anchored on the rock surface (Zhang et al., 2021).

Finite element simulations demonstrated the shutoff effect of silica nanoparticles within the core pores. Fig. 9(b) depicts the meshed model, illustrating its external geometry and internal structure. The model dimensions are 0.5 mm × 0.2 mm × 0.2 mm, containing randomly packed spherical particles. The inter-particle voids serve as the pore channels of the porous medium, facilitating the subsequent simulation of silica nanoparticles transport and shutoff. Fig. 9(c) illustrates the fluid flow direction applied to the mesh prior to computation, along with the X and Y cross-sectional views of the model. Subsequent simulation results visualized the transport trajectories and shutoff behavior of nanoparticles within the pore throats along these cross-sections, providing a theoretical framework for evaluating the shutoff efficiency of silica nanoparticles. Furthermore, Table 7 summarizes key simulation parameters, including empirical values for pore structure properties,

measured values for fluid and nanoparticle properties, and flow rates specified based on displacement conditions.

Fig. 10 clearly illustrates the dynamic process of generation–migration–shutoff–flow and pressure field feedback of silica nanoparticles within the porous medium. As nanoparticles are continuously generated, the interparticle adsorption and the bridging effect at the pore throats are progressively enhanced, establishing a structural foundation for blocking the seepage channels (Fig. 10(a)). The particle migration trajectories exhibit complex, tortuous, and vortex-like patterns, reflecting both the macroscopic guidance by fluid drag forces and local deviations due to phenomena such as Brownian motion (Fig. 10(b)). This extensive interaction with the heterogeneous pore structure facilitates particle retention at the pore throats, providing a kinematic basis for subsequent shutoff. In the fluid velocity field (Fig. 10(c)), the initially dominant orange-red high-velocity regions continuously shrink as particles block the main flow channels, transitioning towards blue-green low-velocity areas. The flow resistance increases significantly due to particle accumulation, leading to a notable attenuation of flow velocity. The coupled pressure field shows a corresponding response (Fig. 10(d)), evolving from an initial clear pressure gradient distribution to a concentration of

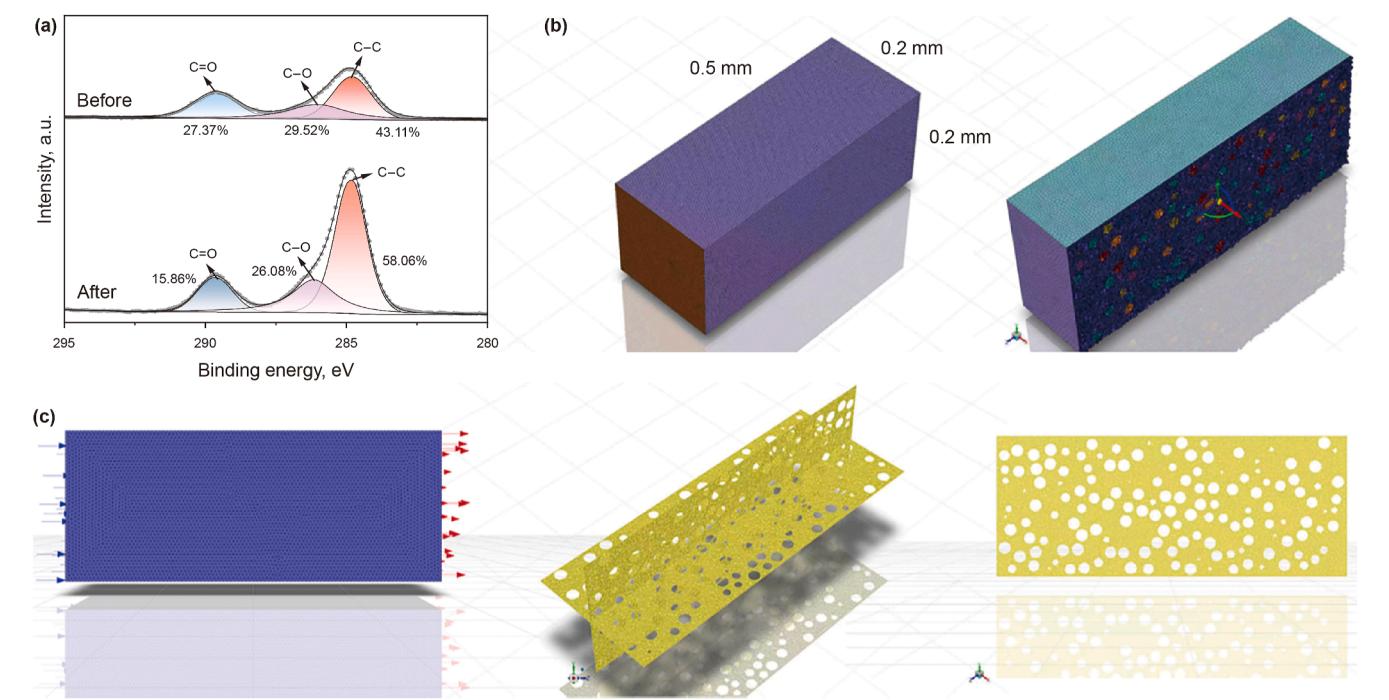


Fig. 9. (a) XPS C 1s spectra of quartz sand surface before and after displacement experiment; (b) mesh delineation results of porous media model; (c) post-processing of the porous media model with the 3D isometric view and corresponding XY cross-section.

Table 7
Parameters applied in simulation.

Porous medium and fluid		Shutoff nanoparticles	
Pore-throat diameter of rock, μm	5–30	Density of shutoff nanoparticles, kg/m^3	2650
Degree of curvature	1.2–2.0	Young's modulus of nanoparticles, N/m^2	5×10^{10}
Fluid density, kg/m^3	996	Friction coefficient	0.3
Fluid viscosity, $\text{kg}/(\text{m}\cdot\text{s})$	0.00095	Spread parameter	3.5
Velocity magnitude, m/s	0.06	Particle size, μm	1–3

orange-red high-pressure zones, indicating that a higher pressure is required for the fluid to break through the porous medium. The dynamic generation and aggregation of particles, the attenuation response of the flow velocity field, and the high-pressure feedback from the pressure field interact and continuously couple, ultimately achieving efficient shutoff of the porous medium. While the idealized geometry of the porous media model precludes direct quantitative comparison with experimental results, the simulated trend of pressure build-up and flow field attenuation (Fig. 10(c) and (d)) are qualitatively consistent with the pressure responses observed during core flooding experiments (Fig. 6(h)). These results validate the effective multi-scale adaptability of the *in situ*-generated SiO_2 nanoparticles to the pore structure and their successful shutoff of heterogeneous reservoirs.

SEM and AFM provided microscopic and nanoscopic evidence. SEM analysis further confirmed the microscopic shutoff state and capability of silica nanoparticles within the pore structure based on the simulation results. As shown in Fig. 11(a), *in situ*-generated SiO_2 nanoparticles aggregated and interconnected during the aging of the emulsion, forming a three-dimensional (3D) porous network. Fig. 11(b) visually demonstrates the shutoff effect of the nanoparticles in the core pores after the displacement experiment. At the $1\ \mu\text{m}$ scale, nanoparticles adhered to the pore walls and throats, forming flocculent aggregates that partially blocked the pore entrances, leading to macro-scale planar shutoff. Under high-magnification at the $300\ \text{nm}$ scale, nanoparticles mutually

adsorbed via interfacial forces, forming a dense 3D network with surface roughness and low porosity. This continuous structure significantly reduced the original pore volume, providing a critical structural foundation for effective shutoff.

AFM characterization elucidated the nanoscale anchoring mechanism underpinning the macroscopic stability. Topographical analysis revealed a continuous surfactant monolayer ($\sim 0.88\ \text{nm}$ thick) on the substrate (Fig. 11(c)). After nanoparticle adsorption, the layer thickness increased to $\sim 2.29\ \text{nm}$ (Fig. 11(d)), confirming successful anchoring. Critically, force-distance curve measurements (Fig. 11(e)) quantified an increase of $\sim 64\%$ in maximum adhesion force (from 16.8 to $27.5\ \text{nN}$) for the surfactant-nanoparticle system compared to the surfactant-only layer.

To validate that this nanoscale adhesion is sufficient for anchoring under flow, we compared it to the estimated hydrodynamic drag force (F_{drag}) on a primary nanoparticle ($\sim 60\ \text{nm}$ radius) under representative seepage condition. The detailed atomic force microscopy force comparison and calculation are provided in Section S8 in Supplementary Material. Using Stokes' law ($F_{\text{drag}} = 6\pi\eta r_p V$), F_{drag} was calculated to be approximately $0.12\ \text{pN}$. The measured AFM adhesion force ($\sim 27.5\ \text{nN}$) is approximately $230,000$ times greater than the drag force, demonstrating that the surfactant-mediated anchoring is robust enough to withstand reservoir flow and ensure long-term shutoff stability (detailed calculations are provided in Section S8 in Supplementary Material).

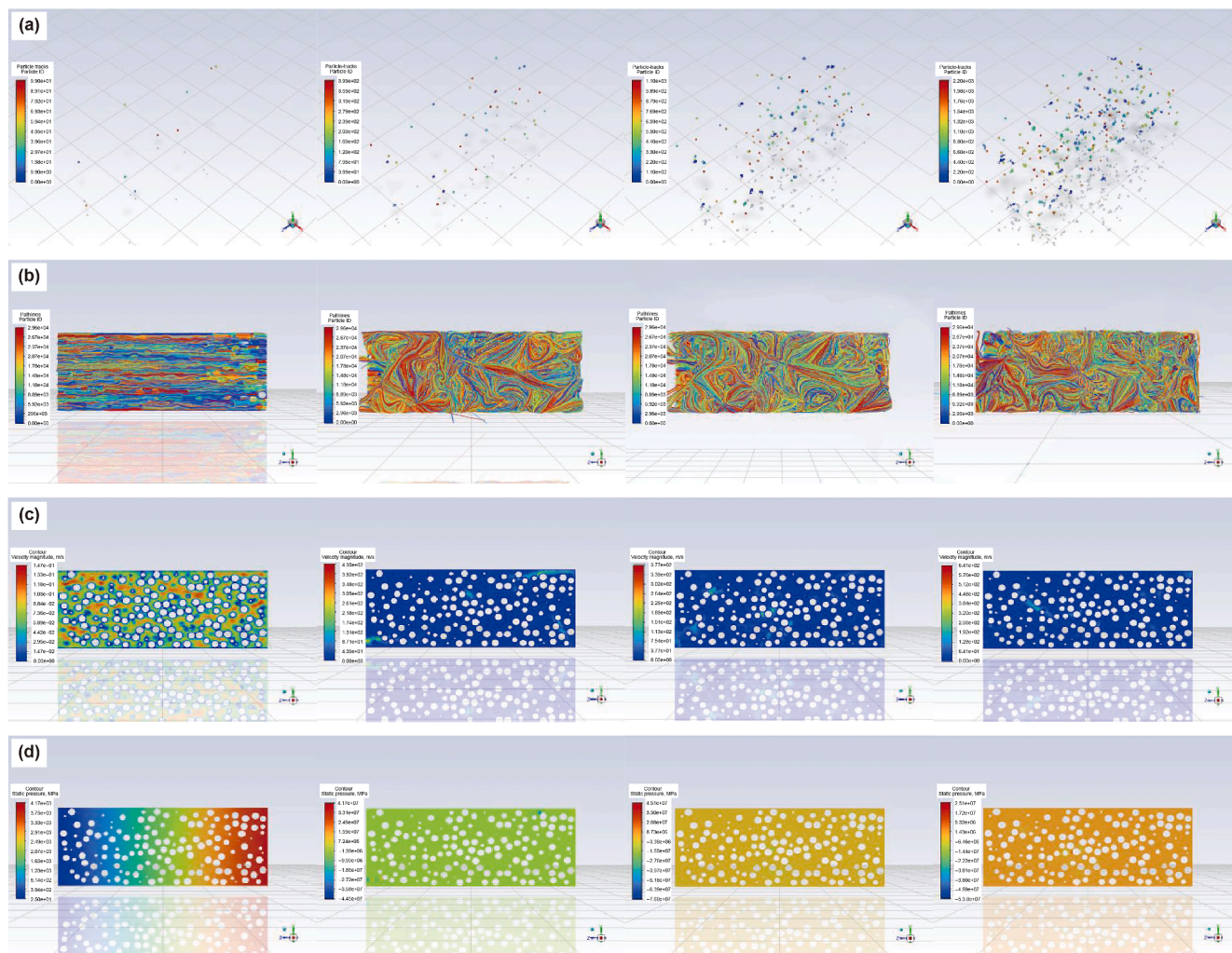


Fig. 10. (a) Dynamic formation and distribution evolution of silica nanoparticles; (b) motion trajectory characteristics of silica nanoparticles; (c) dynamic response of fluid velocity field in porous medium; (d) dynamic feedback characteristics of pressure field in porous medium.

Combining all evidence, the shutoff process follows a coherent three-stage mechanism (Fig. 12). (1) Surfactant adsorption: Upon emulsion breakdown, released surfactants adsorb onto the rock surface via hydrogen bonding and electrostatic interactions, forming a hydrophobic monolayer and providing active sites. (2) Network formation: *In situ*-generated SiO_2 nanoparticles aggregate through van der Waals forces and bridging, forming a 3D porous network that physically obstructs pore throats. (3) Synergistic anchoring: The adsorbed surfactant layer acts as a functional interface, where its hydrocarbon chains entangle with nanoparticles via hydrophobic interactions, significantly enhancing adhesion (as quantified by AFM) and securing the plugging network against hydrodynamic forces. This multi-scale mechanism—from molecular adsorption to nanoparticle aggregation and micro-plugging—explains the high-efficiency, selective, and stable water shutoff performance achieved by the *in situ*-generated silica nanonetwork system.

3.5. Comparison with conventional nanoparticle-based EOR systems

To further highlight the innovation and practical advantages of the *in situ* silica nanonetwork strategy proposed in this work, a systematic comparison with conventional pre-synthesized

nanoparticle systems is presented in Table 8. Conventional systems often face challenges such as irreversible aggregation during migration, poor size matching with heterogeneous pore throats, and complex preparation processes involving surface modification or external catalysts. In contrast, our approach employs an emulsion-templated *in situ* formation mechanism, which fundamentally avoids migration-induced aggregation. Moreover, the glycerol-mediated dielectric tuning enables precise control over nanoparticle size and aggregation state, ensuring effective shutoff across a range of permeabilities. The surfactant system also serves a dual role, eliminating the need for additional catalysts or post-synthesis modification, thereby simplifying the formulation and reducing energy and chemical inputs. This comparison underscores a novel strategy that addresses the long-standing migration-aggregation dilemma of pre-synthesized nanoparticles, which transitions from delivering pre-made nanoparticles to triggering their formation within the target reservoir zones, thereby offering a more efficient, adaptable, and energy-conscious solution for conformance control.

In terms of energy efficiency, quantitative calculation of the core operational pumping energy (the dominant energy consumption in EOR field operations) under standard oilfield conditions further verifies the outstanding advantages of this system.

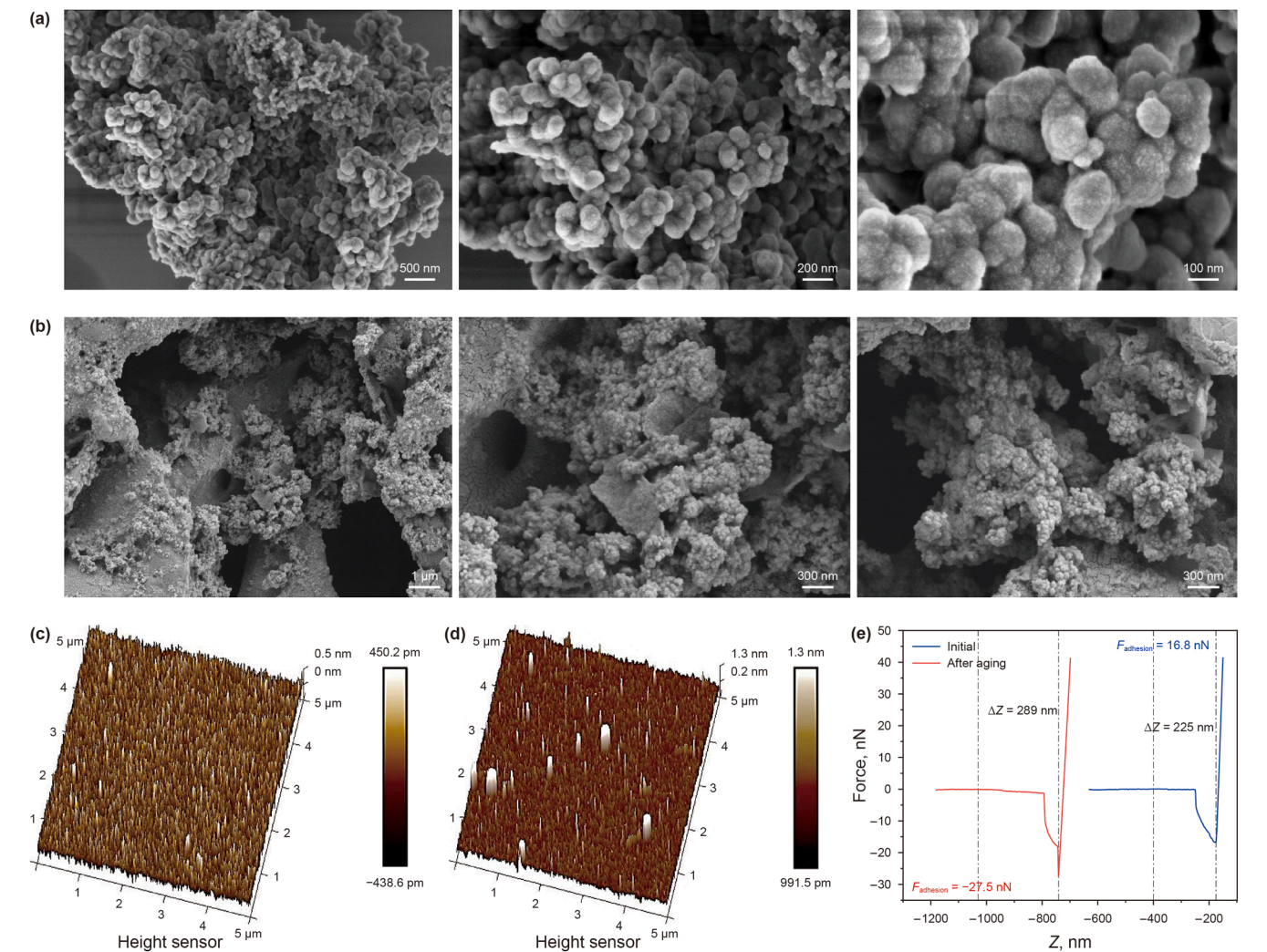


Fig. 11. (a) SEM images of SiO₂ nanoparticles; (b) SEM images of silica nanoparticle network formed in core pores; (c-e) AFM characterization of surfactant–nanoparticle synergistic anchoring effect.

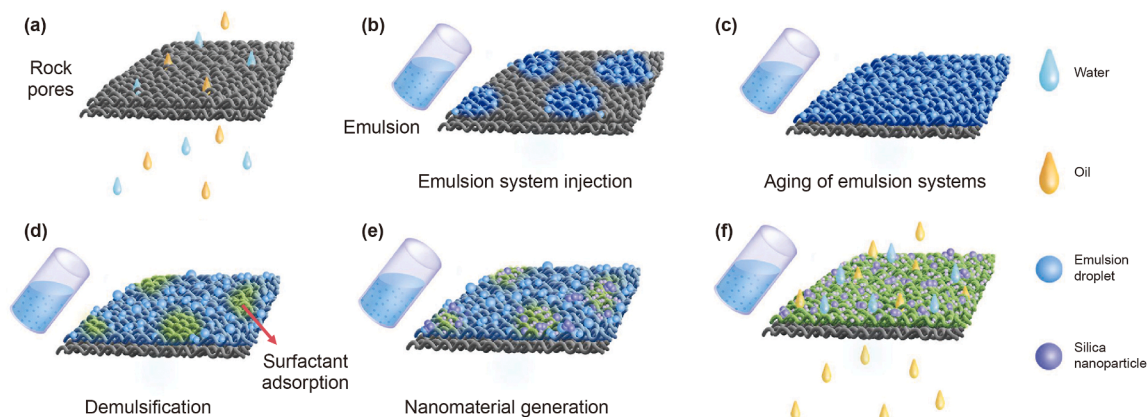


Fig. 12. Emulsion system shutoff process.

Table 8
Comparison between *in situ*-formed SiO₂ nanonetwork strategy and conventional pre-synthesized nanoparticle EOR systems.

Aspect	Conventional pre-synthesized nanoparticle systems (Li et al., 2023; Luo et al., 2022; Xing et al., 2025; Xue et al., 2024)	This work
Nanoparticle delivery	Pre-synthesized and injected; prone to aggregation/retention during migration	Injected as an emulsion; nanoparticles form <i>in situ</i> within reservoir pore throats, avoiding migration-induced aggregation
Size control mechanism	All have failed to consider the influence of particle size and distribution on plugging performance, making it difficult to dynamically adapt to heterogeneous pore structures	Glycerol tunes medium polarity, allowing precise control of SiO ₂ primary size and aggregation state to match varying permeability zones
Cost and process complexity	Often involves complex surface modification, purification, organic solvents, or external catalysts	No external acid/base catalysts are required; surfactants serve dual roles; simple and environmentally friendly process

Based on the classic hydraulic power formula, the energy consumption of the pump can be expressed as follows:

$$E = \frac{PQt}{\eta_{\text{pump}}} \tag{6}$$

where E is the pumping energy, J; P is the injection pressure, Pa; Q is the flow rate, m³/s; t is the injection time, s; and η_{pump} is the pump efficiency (taken as 0.85) under the same application conditions (injecting 10 m³ working fluid into an approximately 500 mD medium-to high-permeability reservoir at an injection flow rate of 1 mL/min).

Based on the classic hydraulic power formula, the pumping energy consumption of our system (0.02 MPa injection pressure) is only 235.34 kJ. In comparison, the conventional pre-synthesized nanoparticle emulsion system (1.5 MPa injection pressure) and polymer gel system (1.2 MPa injection pressure) exhibit pumping energy consumptions of 17,650.588 and 14,120.47 kJ, respectively. This translates to a 98.7% pumping energy saving compared with the pre-synthesized nanoparticle emulsion systems and a 98.3% saving compared with the polymer gel systems. The remarkable energy-saving effect stems from the ultra-low viscosity of the emulsion precursor and the fundamental elimination of near-wellbore clogging, which avoids the high injection pressure caused by the migration-aggregation of pre-synthesized nanoparticles and by the intrinsic high viscosity of polymer gels (Luo et al., 2026; Wang et al., 2024a).

This comparison underscores the key advantages of the proposed strategy, which represents a fundamental shift from delivering pre-fabricated nanoparticles to enabling their *in situ* generation directly within target reservoir zones. This approach offers a more efficient, adaptable, and energy-conscious technical solution for water shutoff applications.

4. Conclusions

This study successfully developed an emulsion system for enhanced oil recovery by enabling the *in situ* synthesis of silica nanonetworks within reservoir pore throats. This strategy addresses the long-standing migration-aggregation dilemma of pre-synthesized nanoparticles. The core innovation is a surfactant-driven, additive-free synthesis where the surfactant serves a dual role: Upon demulsification, it promotes TEOS hydrolysis-condensation by reducing the interfacial energy barrier, while simultaneously adsorbing onto nascent silica to impart hydrophobicity, establishing the foundation for selective water shutoff.

Precise control over nanoparticle size and aggregation, which is critical for matching heterogeneous permeability zones, was achieved by glycerol-mediated dielectric tuning of the reaction microenvironment. This integrated approach resolves the migration-aggregation dilemma. The synergy between surfactant

adsorption on the rock surface and nanoparticle physical bridging forms a robust three-dimensional shutoff network. Displacement experiments validated exceptional performance, achieving water shutoff efficiency of over 90%, while maintaining oil-phase permeability retention above 70% in cores with initial permeabilities spanning 100–1000 mD. The system's ultra-low viscosity (<1.5 mPa·s), thermal stability, and shear resistance ensure excellent injectability, and it realizes a 98.3%–98.7% reduction in pumping energy consumption compared with conventional systems, translating to tangible energy efficiency advantages for field application.

From an environmental and operational perspective, the system presents a favorable profile. The hydrolysis byproduct (ethanol) is minimal and diluted *in situ*, and the surfactants used exhibit good biodegradability. Combined with the high material utilization efficiency of the *in situ* process, this strategy aligns with the goals of sustainable hydrocarbon production. Overall, this *in situ* synthesis method provides a customizable and efficient solution for improving sweep efficiency, representing a significant advance toward more energy-efficient and environmentally considerate enhanced oil recovery.

CRediT authorship contribution statement

Yi-An Zhao: Writing – original draft, Methodology, Investigation, Formal analysis, Conceptualization. **Xun Qi:** Validation, Formal analysis. **Su-Chen Xiao:** Validation, Methodology, Investigation. **Zhang Luo:** Validation, Investigation. **Yun-Long Liu:** Validation, Resources. **Tian-Jiang Wu:** Validation, Resources. **Jie Wen:** Writing – review & editing, Supervision. **Cai Chen:** Writing – review & editing, Supervision, Software, Formal analysis. **Hui Zhang:** Writing – review & editing, Validation, Resources, Project administration, Methodology, Funding acquisition, Data curation, Conceptualization.

Data availability

Data will be made available on request.

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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Supplementary data

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