

Preparation and enhanced oil recovery mechanism of dual-shell amphiphobic fluorinated nano-polymer core–shell materials

Research Article

Guojie Sui¹, Hai Lin¹, Huan Liu¹, Tingsong Xiong¹, Shiduo Liu¹, Shijun Chen^{2*}

¹ Oil and Gas Technology Research Institute, PetroChina Qinghai Oilfield Company, Dunhuang, 736202, China

² College of Chemistry and Chemical Engineering, Xi'an Shiyou University, Xi'an, 710065, China

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Abstract: This study developed dual-shell amphiphobic fluorinated polymer core–shell materials (AFPCSMs) for wettability alteration in tight oil reservoirs. The materials comprise silica nanoparticle cores (30 nm), γ -aminopropyltriethoxysilane methacrylic anhydride inner shells, and fluorinated polymer outer shells via 2,2,2-trifluoroethyl methacrylate dodecafluoroheptyl methacrylate copolymerization. Fourier transform infrared spectrometer, X-ray photoelectron spectroscopy, and thermogravimetric analyzer characterization confirmed successful dual-shell construction. AFPCSMs achieved superior amphiphobic properties with water contact angles of 145.3°, *n*-hexadecane contact angles of 132.6°, and surface free energy reduction to 1.44 mN/m (95.7% decrease). Stability tests demonstrated excellent retention rates: 92.1% thermal stability at 120°C, 94.7% salt resistance under 25,000 mg/L salinity, and 91.1% durability after 72-h flooding. Core flooding experiments showed enhanced oil recovery of 71.52% with 36.05 percentage points net increase (101.6% relative enhancement) and lowest pressure gradient (0.85 MPa/PV). Comparative studies confirmed the dual-shell design's superiority over single-shell materials across all evaluation criteria, providing an effective approach for precision wettability control in challenging reservoir applications.

Keywords: Dual-shell nanoparticles • Wettability alteration • Enhanced oil recovery • Fluorinated polymers

1. Introduction

With the advancement of petroleum industry development, low-permeability and tight hydrocarbon reservoirs have emerged as focal points for unconventional resource exploitation [1–3]. These reservoir formations commonly exhibit characteristics of fine pore-throat structures and strong water-wet properties, resulting in elevated capillary resistance and poor sweep efficiency during water-flooding operations, severely constraining development effectiveness [4]. Wettability modification technology, as a critical enhanced oil recovery technique, has garnered extensive attention in recent years [5–7].

Nanomaterials demonstrate tremendous potential in reservoir wettability alteration owing to their distinctive surface effects and size-dependent properties [8,9]. Silica

nanoparticles possess advantageous characteristics including large specific surface areas, abundant surface hydroxyl groups, and excellent chemical stability, making them ideal carriers for functionalized nanomaterial synthesis [10,11]. However, conventional single-shell modification strategies present numerous limitations: inadequate functional group exposure, tendency toward aggregation in high-salinity formation brines, and insufficient thermal stability requirements [12,13].

Addressing these challenges, this investigation innovatively proposes a dual-shell design concept: utilizing nanosilica as a rigid core, constructing a stable chemical bonding layer through silane coupling agents as the inner shell, and grafting fluorinated polymers as the outer shell to achieve wettability modification functionality. The dual-shell architecture offers several theoretical advantages over conventional single-shell designs: (1) the inner shell (APTES-MANh) provides robust covalent bonding to the

* E-mail: csj19792018@sina.com

silica core through Si–O–Si linkages while introducing polymerizable vinyl groups for subsequent polymer grafting; (2) the outer fluorinated polymer shell delivers low surface energy functionality through abundant $-\text{CF}_2-$ and $-\text{CF}_3$ groups; (3) the interlayer synergistic effects enable stress transfer and thermal buffering, where the flexible inner shell accommodates thermal expansion mismatch between the rigid silica core and the polymer outer shell, thereby enhancing overall structural integrity under harsh reservoir conditions. This stratified design not only maximizes the advantages of individual components but also significantly enhances overall material performance through interlayer synergistic effects. Through systematic comparative experimentation, the technical superiority of the dual-shell design relative to conventional single-shell architectures was validated, providing novel solutions for precision reservoir wettability control.

2. Experimental section

2.1 Experimental materials

Nano-silica (SiO_2 , average particle diameter 30 nm, specific surface area $300 \text{ m}^2/\text{g}$, purity 99.8%) was procured from Shanghai Aladdin Biochemical Technology Co., Ltd; γ -aminopropyltriethoxysilane (APTES, 99%) was procured from Beijing Bailingwei Technology Co., Ltd; methacrylic anhydride (MANh, 99%) was obtained from Sigma-Aldrich (Shanghai) Trading Co., Ltd; perfluorooctyl trichlorosilane (PFOTS, 98%) was obtained from Shanghai Macklin Biochemical Technology Co., Ltd; 2,2,2-trifluoroethyl methacrylate (TFEMA, 96%) and dodecafluoroheptyl methacrylate (DFHMA, 96%) were procured from Harbin Xeogia Fluorine-Silicon Chemical Co., Ltd. ammonium persulfate (APS, analytical grade), N,N -dimethylformamide (DMF, analytical grade), tetrahydrofuran (THF, analytical grade), anhydrous ethanol (analytical grade), etc., were procured from Sinopharm Chemical Reagent Co., Ltd. Experimental water was deionized water (resistivity $>18.2 \text{ M}\Omega \text{ cm}$).

2.2 Dual-shell nanomaterial synthesis

The preparation of dual-shell nanomaterials encompasses three sequential steps: silica core pretreatment, inner shell formation, and outer shell construction, as illustrated in Figure 1.

2.2.1 Silica core pretreatment

5.0 g of nano-silica was dispersed in 150 mL of anhydrous ethanol and ultrasonicated for 45 min. 10 mL of 10% ammonia solution was added to adjust pH to 9–10, followed by 30 min stirring for surface activation. The product was isolated by centrifugation, washed with deionized water until neutral, subsequently washed three times with ethanol, and dried at 80°C for 12 h.

2.2.2 Inner shell formation

Step 1: 4.5 g of activated silica was dispersed in 100 mL of toluene, and APTES solution (3.0 mL dissolved in 25 mL of toluene) was dropwise added at 110°C , followed by 6 h reaction. The aminofunctionalized product was obtained after washing and drying. Chemical reaction equations are shown in Figure 2.

Step 2: The product was dispersed in 80 mL THF, MANh solution (1.5 g) was added under ice-bath conditions, then heated to 40°C for 4 h reaction to introduce polymerizable double bonds. Inner shell material was obtained after washing and drying. Chemical reaction equations are presented in Figure 3.

2.2.3 Outer shell formation

2.5 g of inner shell material was dispersed in 80 mL of DMF, and APS initiator (0.4 wt%) was added at 75°C . Fluorinated monomer mixture (TFEMA 0.8 g + DFHMA 1.2 g) was added dropwise using a peristaltic pump over 2 h, followed by continued reaction for 3.5 h to obtain amphiphobic fluorinated polymer core-shell materials (AFPCSMs). Chemical reaction equations are shown in Figure 4.

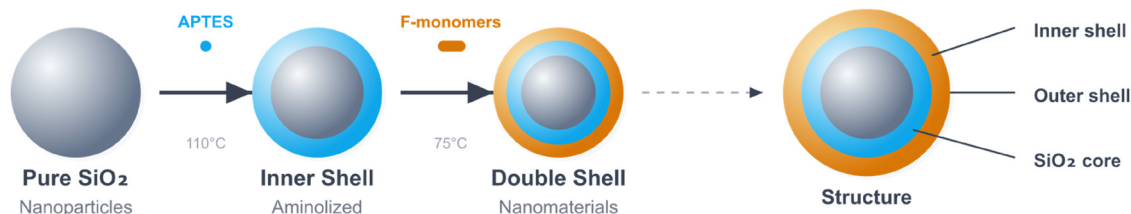


Figure 1. Synthesis procedure of dual-shell nanomaterials.

Source: Author's contribution.

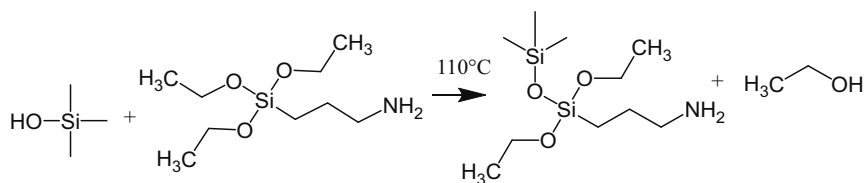


Figure 2. Chemical reaction equations for Step 1.

Source: Author's contribution.

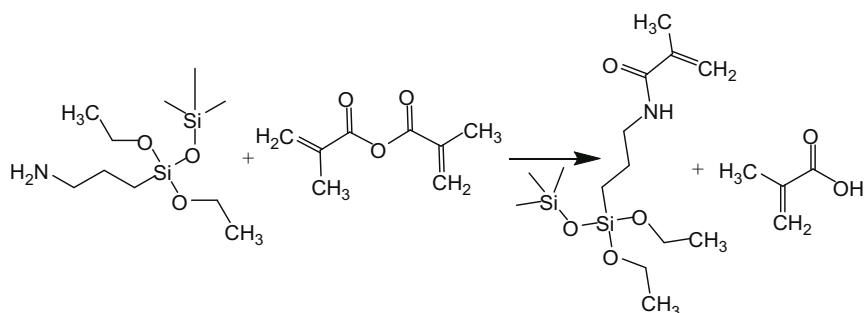


Figure 3. Chemical reaction equations for Step 2.

Source: Author's contribution.

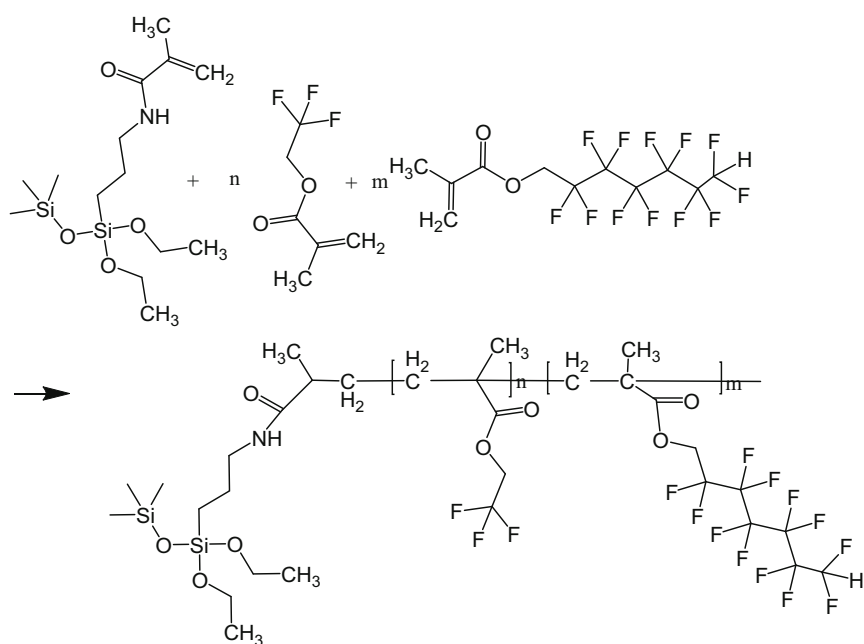


Figure 4. Chemical reaction equations for shell layer preparation.

Source: Author's contribution.

2.2.4 Product isolation

Upon reaction completion, the product was sequentially washed with DMF, ethanol, and deionized water, dried at 60°C for 24 h, followed by 80°C for 24 h to yield white powdered dual-shell nanomaterials.

2.2.5 Comparative material preparation

To validate the advantages of dual-shell design, the following comparative materials were synthesized: Single-shell material-B (APTES-MANh): Silica modified only with APTES and MANh; Single-shell material-C (C-PFOTS): Single-shell core-shell material based on PFOTS. The overall yield of AFPCSMs was $76.5 \pm 3.2\%$ ($n = 3$) based on initial silica mass. Individual step yields were activated silica 94.2%, inner shell formation 89.3%, and outer shell grafting 91.0%. The moderate yield is attributed to cumulative losses during multiple washing and centrifugation cycles.

2.3 Characterization methods

Fourier transform infrared spectrometer (FTIR, Bruker Vertex 70) for chemical structure analysis, X-ray photoelectron spectroscopy (XPS, Thermo Fisher ESCALAB 250Xi) for surface elemental composition analysis, thermogravimetric analyzer (TGA, PerkinElmer TGA 4000) for thermal stability evaluation, and contact angle measuring instrument (OCA 20, DataPhysics, Germany) for wettability determination were utilized.

2.4 Performance evaluation methods

2.4.1 Wettability assessment

Natural sandstone cores ($\phi 2.5 \text{ cm} \times 5.0 \text{ cm}$, permeability $\sim 750 \text{ mD}$, porosity 22%) were selected and subjected to the following pre-treatment procedure: (1) Soxhlet extraction with toluene for 48 h to remove residual hydrocarbons, (2) sequential washing with methanol and deionized water, (3) drying at 105°C for 24 h in a vacuum oven, and (4) cooling in a desiccator to room temperature. The pre-treated cores were then saturated with different material solutions under vacuum for 2 h, followed by atmospheric soaking for 12 h. Treatment concentration ranged from 0.01–0.20 wt%. After treatment, cores were dried at 80°C for 4 h before measurements. Static contact angles with

deionized water and *n*-hexadecane were measured before and after treatment using the sessile drop method, with eight measurements at different positions averaged for each sample. Surface free energy was calculated using the Owens–Wendt–Rabel–Kaelble (OWRK) method with two probe liquids: deionized water ($\gamma L = 72.8 \text{ mN/m}$) and diiodomethane ($\gamma L = 50.8 \text{ mN/m}$). The total surface free energy (γ_s) was determined as the sum of dispersive (γ_s^d) and polar (γ_s^p) components using the equation: $\gamma L(1 + \cos\theta) = 2[(\gamma_s^d \gamma L^d)^{0.5} + (\gamma_s^p \gamma L^p)^{0.5}]$.

2.4.2 Stability assessment

2.4.2.1 Thermal stability testing

Treated cores were maintained at different temperatures (60, 80, 100, and 120°C) for 24 h, and contact angle variations were measured.

2.4.2.2 Salt resistance testing

Cores were treated in formation brines of different salinities (5,000, 15,000, 25,000 mg/L NaCl solutions) to evaluate the impact of salt ions on wettability modification effectiveness.

2.4.2.3 Durability testing

Treated cores underwent long-term waterflooding erosion (flow rate 2 mL/min, duration 72 h) with periodic contact angle measurements.

2.4.3 Displacement performance evaluation

One-dimensional sand-pack displacement apparatus was employed for systematic evaluation of dual-shell fluorinated nanocomposite displacement performance. The experimental setup included precision injection pumps for sequential fluid injection, real-time pressure monitoring systems, and temperature-controlled sand-pack models ($\phi 2.5 \times 30 \text{ cm}$) filled with 40–60 mesh quartz sand. Standard displacement experimental procedure: (1) Vacuum saturation with formation brine to establish connate water saturation, (2) Oil saturation with *n*-octane to achieve initial oil saturation, (3) Waterflooding to 95% water cut to determine baseline recovery, (4) Injection of 0.5 pore volumes (PVs) of chemical solution (0.05 wt% concentration) followed by 12-h shut-in, and (5) Continued waterflooding until pressure stabilization. All experiments were conducted at 70°C with injection rate of 0.3 mL/min. Experimental apparatus and procedure are shown in Figure 5.

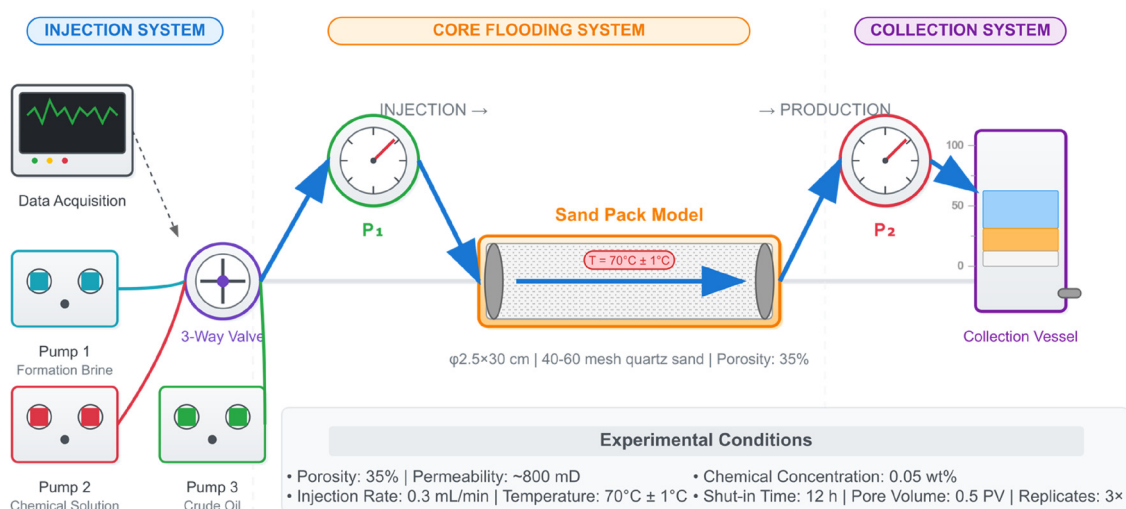


Figure 5. Schematic diagram of experimental apparatus for displacement performance evaluation.

Source: Author's contribution.

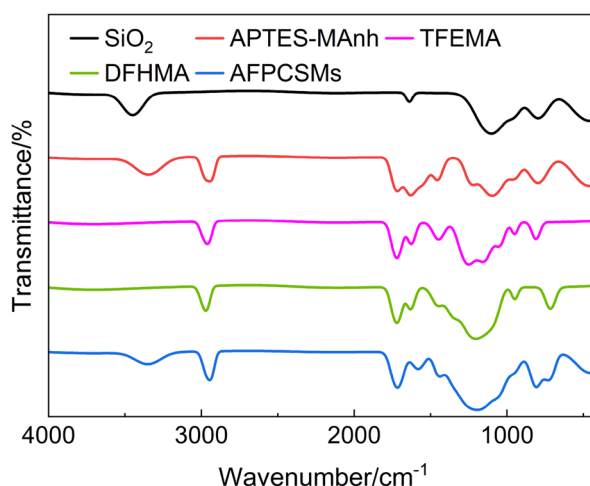


Figure 6. FTIR spectroscopy spectrum.

Source: Author's contribution.

3. Results and discussion

3.1 Material structural characterization

3.1.1 FTIR analysis

The successful construction of the dual-shell architecture was confirmed by FTIR spectroscopy, as shown in Figure 6. FTIR spectra of pristine SiO_2 nanoparticles and the synthesized dual-shell AFPCSMs were comparatively analyzed to validate the stepwise functionalization process.

3.1.1.1 Pristine SiO_2 baseline

The spectrum of unmodified silica exhibited characteristic absorption bands at $3,450\text{ cm}^{-1}$ (O–H stretching [14]), $1,100\text{ cm}^{-1}$ (Si–O–Si asymmetric stretching [15]), and 800 cm^{-1} (Si–O–Si symmetric stretching), confirming abundant surface hydroxyl groups available for subsequent modification.

3.1.1.2 Dual-shell structure validation

The FTIR spectrum of synthesized AFPCSMs provided definitive evidence for successful dual-shell construction:

3.1.1.2.1 Inner shell confirmation

The emergence of a distinct peak at $1,580\text{ cm}^{-1}$, attributed to N–H bending vibration [16], confirmed the successful grafting of APTES onto the silica surface. C–H stretching vibrations at $2,920\text{--}2,970\text{ cm}^{-1}$ further evidenced the presence of aminopropyl chains [17].

3.1.1.2.2 Outer shell verification

Intense absorption bands at $1,240\text{ cm}^{-1}$ (CF_2 stretching [18]) and $1,180\text{ cm}^{-1}$ (C–F stretching) definitively confirmed the successful polymerization and grafting of fluorinated polymer chains [19]. The simultaneous presence of CF_3 characteristics at $1,150\text{ cm}^{-1}$ (from TFEMA) and CF_2 chain signatures at $1,200\text{--}1,250\text{ cm}^{-1}$ (from DFHMA) indicated the formation of the intended copolymer outer shell.

3.1.1.2.3 Structural integrity

The preservation of Si–O–Si vibrations at $1,100$, 800 , and 460 cm^{-1} , albeit with reduced intensity due to surface coverage, confirmed that the silica core remained structurally intact throughout the multi-step functionalization. Peak broadening in the $1,100\text{ cm}^{-1}$ region, resulting from the overlap of Si–O–Si and C–F stretching modes, is characteristic of extensively functionalized core–shell nanocomposites.

The FTIR analysis provided unambiguous spectroscopic evidence for the successful construction of the dual-shell architecture, with both aminosilane inner shell and fluorinated polymer outer shell components clearly identified while maintaining core structural integrity.

3.1.2 XPS analysis

XPS analysis provided quantitative confirmation of the dual-shell architecture construction, as illustrated in Figure 7. Surface elemental composition revealed dramatic changes upon stepwise functionalization: Si content decreased progressively from 28% (pristine SiO_2) to 22% (APTES-MANh) to 13% (AFPCSMs), while carbon content increased correspondingly from 5% to 18% to 38%. Most significantly, the emergence of fluorine signal at 15 atomic% in AFPCSMs constituted definitive evidence for successful fluorinated polymer grafting, while retained nitrogen signal (2–3%) confirmed preservation of the APTES inner shell (Table 1).

Core-level spectral analysis provided detailed chemical environment information. Si 2p spectra maintained the characteristic doublet at $\sim 103.4\text{ eV}$ for all materials, confirming SiO_2 framework preservation with systematic intensity reduction reflecting increasing surface coverage

[20]. C 1s spectra exhibited substantial evolution from minimal adventitious carbon in pristine SiO_2 to complex multi-component profiles in AFPCSMs, displaying aliphatic polymer carbons (285 eV), fluorinated carbons (287 eV), and ester carbonyls (289 eV) [21]. N 1s analysis demonstrated stable amide linkage retention, with peaks at 401.0 eV (APTES-MANh) and 400.8 eV (AFPCSMs) [22]. F 1s spectra revealed a characteristic peak at 689.5 eV, confirming C–F bond formation in the fluorinated polymer shell [23]. O 1s spectra exhibited systematic chemical shifts from 532.7 eV (SiO_2) to 532.6 eV (APTES-MANh) to 531.7 eV (AFPCSMs) [24]. The significant 1.0 eV negative shift in AFPCSMs indicates substantial changes in oxygen chemical environment due to extensive organic layer formation and ester bond creation.

The XPS data collectively validated successful dual-shell construction through multiple lines of evidence: 15% fluorine content confirmed polymer grafting efficiency, 54% silicon signal reduction demonstrated effective surface coverage, and the observed C/F atomic ratio ($\sim 2.5:1$) aligned with theoretical TFEMA-DFHMA copolymer composition. These results establish the chemical integrity of each functional layer and confirm the dual-shell architecture design.

3.1.3 TGA analysis

Thermogravimetric analysis results are presented in Figure 8, where thermal decomposition profiles of the three materials exhibit distinctly different stages, reflecting their unique structural characteristics and chemical compositions. Decomposition temperatures at 5% weight loss were: APTES-MANh 184°C , C-PFOTS 202°C , AFPCSMs 183°C , with onset decomposition temperatures directly correlated to the bond energy of the weakest chemical bonds in each material.

APTES-MANh displayed typical single-stage decomposition characteristics, with concentrated weight loss occurring in the $200\text{--}300^\circ\text{C}$ temperature range [25]. The derivative thermogravimetry (DTG) curve showed a single sharp decomposition peak at 250°C , corresponding to synergistic rupture of C–N bonds and amide linkages. After 68% total weight loss, the remaining mass stabilized at 32%, primarily representing the silica core.

C-PFOTS demonstrated excellent thermal stability with decomposition concentrated in the $280\text{--}350^\circ\text{C}$ range. The DTG peak appeared at 300°C , corresponding to Si–C bond cleavage and perfluorooctyl chain detachment. Following complete decomposition, approximately 25% residual mass remained, with 75% weight loss primarily attributed to high molecular weight perfluoroalkyl chains.

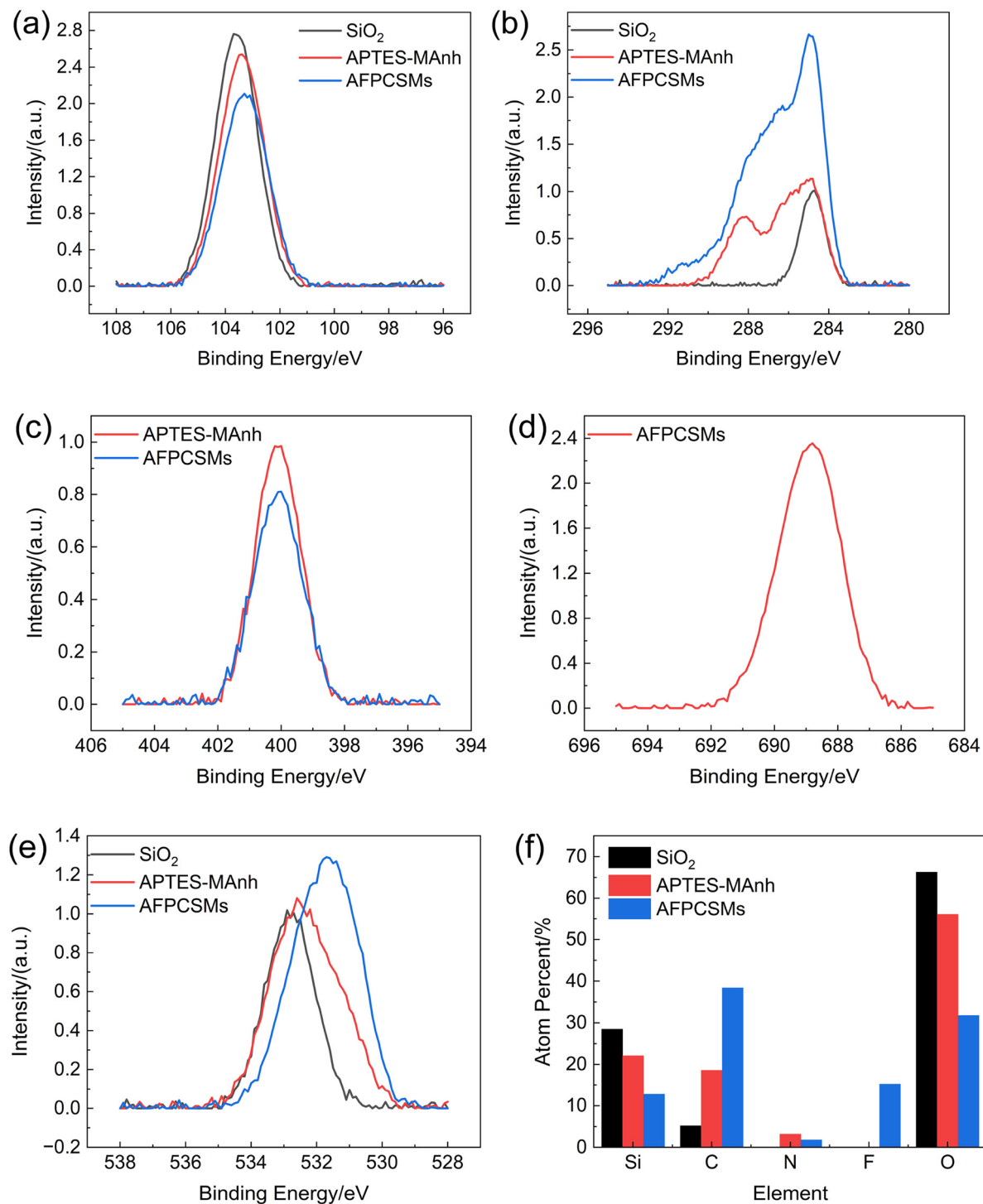


Figure 7. XPS characterization of dual-shell amphiphobic fluorinated nanocomposites. (a) Si 2p spectra; (b) C 1s spectra; (c) N 1s spectra; (d) F 1s spectra; (e) O 1s spectra; and (f) surface elemental composition (atomic percentage).

Source: Author's contribution.

Table 1. Surface elemental composition determined by XPS (atomic %)

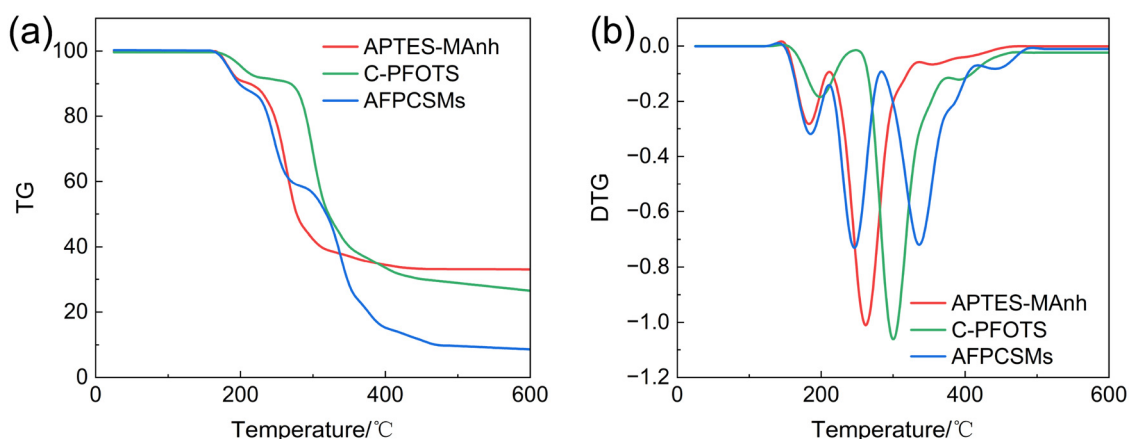
Material	Si	O	C	N	F
Pristine SiO ₂	28.3	66.8	4.9	—	—
APTES-MAnh	22.1	56.7	18.2	3.0	—
AFPCSMs	12.8	32.1	37.6	2.3	15.2

Source: Author's contribution.

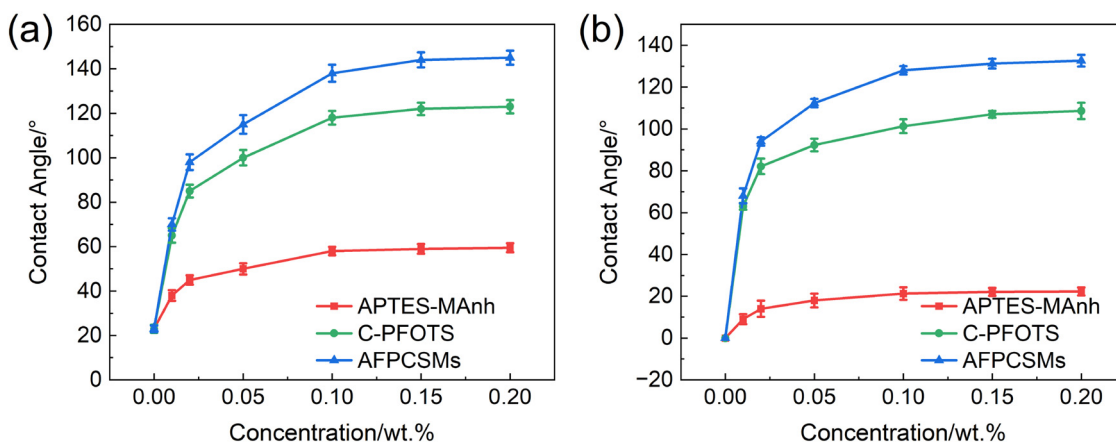
AFPCSMs exhibited complex multi-stage decomposition behavior, with the entire decomposition process divisible into four stages: 180–220°C (surface volatiles, 5% weight loss), 220–280°C (APTES inner shell decomposition,

15% weight loss), 280–380°C (polymer backbone decomposition, 40% weight loss), 380–550°C (fluorinated side chain decomposition, 32% weight loss) [26]. Final residual mass was only 8%, indicating absolute dominance of organic components. The DTG curve displayed multiple separated decomposition peaks, directly validating the existence of dual-shell architecture.

Thermal stability ranking was as follows: AFPCSMs < APTES-MAnh < C-PFOTS. Notably, decomposition onset temperatures for all materials significantly exceeded typical reservoir temperature ranges (60–150°C), indicating adequate thermal stability margins for maintaining structural integrity and functional stability during long-term service in actual hydrocarbon reservoir environments.

**Figure 8.** TGA results: (a) TG and (b) DTG.

Source: Author's contribution.

**Figure 9.** Contact angle measurements of core samples treated with different materials: (a) Contact angle with water and (b) contact angle with *n*-hexadecane. Error bars represent standard deviation ($n = 8$).

Source: Author's contribution.

3.2.3.2 Comparative wettability modification performance

3.2.1 Concentration effect comparison

Contact angle measurements of cores treated with three core-shell materials against water and *n*-hexadecane are presented in Figure 9. Concentration effect analysis revealed distinct differences in wettability modification capabilities as concentration increased. For water contact angle testing, APTES-MANh showed limited hydrophobic capability with contact angles increasing slowly from 38.2° to 59.3° as concentration increased from 0.01 to 0.20 wt%, representing a maximum increase of approximately 21° while maintaining hydrophilic characteristics throughout. C-PFOTS demonstrated significant concentration dependence, with water contact angles increasing rapidly from 65.3° to 123.5°, achieving hydrophobic-to-hydrophobic transition at 0.05 wt% concentration (100.3°). AFPCSMs exhibited optimal wettability modification performance, reaching 70.1° water contact angle at 0.01 wt% concentration, achieving superhydrophobic state (138.2°) at 0.10 wt%, and continuously increasing to 145.3° at 0.20 wt% concentration. The superior performance of AFPCSMs at low concentrations (0.01 wt%) can be attributed to several molecular-level factors: (1) the high density of fluorinated functional groups ($-CF_2-$ and $-CF_3$) on the outer shell surface maximizes per-particle modification efficiency, (2) the dual-shell architecture prevents nanoparticle aggregation through steric stabilization, ensuring uniform dispersion and effective surface coverage, and (3) the covalently bonded APTES-MANh inner shell provides multiple anchoring sites through Si-O-Si linkages to rock surfaces, significantly enhancing adhesion compared to physically adsorbed single-shell materials.

N-hexadecane contact angle testing further confirmed significant material differences. APTES-MANh showed virtually no oleophobic properties with maximum contact angles reaching only 22.3°, confirming absence of oil-repelling functionality. C-PFOTS achieved *n*-hexadecane contact angles exceeding 82.1° at 0.02 wt% concentration, ultimately reaching 108.6°, demonstrating effective oleophobic

performance. AFPCSMs displayed excellent amphiphobic characteristics within the same concentration range, with *n*-hexadecane contact angles reaching 128.4° at 0.10 wt% concentration, achieving maximum values of 132.6°, demonstrating superior oil-repelling capability.

Surface free energy analysis further quantified wettability modification effectiveness, as shown in Table 2. APTES-MANh surface free energy decreased from 59.72 mN/m to 45.78 mN/m, representing only 23.4% reduction, indicating limited surface modification effectiveness. C-PFOTS demonstrated significant surface energy reduction from 37.18 to 6.20 mN/m, achieving 83.3% decrease, confirming fluorination modification effectiveness. AFPCSMs exhibited the most exceptional surface energy modification capability, decreasing from 33.10 to 1.44 mN/m with 95.7% reduction, achieving ultra-low surface energy state at 0.10 wt% concentration. Substantial surface free energy reduction directly corresponds to superior amphiphobic performance, where low surface energy signifies significantly weakened liquid spreading tendency on solid surfaces, thereby achieving hydrophobic and oleophobic functional objectives.

Concentration effect analysis revealed that AFPCSMs achieve effective wettability modification at extremely low concentrations, demonstrating clear concentration advantages over single-shell materials. This advantage primarily stems from high surface functional group density and stable anchoring mechanisms provided by dual-shell structures [27]. Surface free energy data highly correlates with contact angle measurements, collectively validating AFPCSMs' significant advantages in wettability modification and providing reliable theoretical foundation for reservoir modification applications.

3.2.2 Stability performance comparison

Based on performance data at 0.1 wt% concentration, systematic stability evaluation of three materials was conducted, with results shown in Figure 10. Stability testing encompassed three dimensions: thermal stability, salt resistance, and durability, quantitatively assessing material performance stability under different environmental conditions through contact angle retention rates.

Thermal stability testing revealed varying degrees of performance degradation as temperature increased from 60 to 120°C, with significant differences in degradation extent among materials. As shown in Figure 10(a), APTES-MANh demonstrated relatively poor thermal stability with water contact angle retention rate of only 78.6% at 120°C conditions, primarily attributed to thermal degradation of

Table 2. Surface free energy of rocks with different materials

Material	0.01 wt%	0.05 wt%	0.10 wt%
APTES-MANh	59.72 mN/m	51.46 mN/m	45.78 mN/m
C-PFOTS	37.18 mN/m	12.79 mN/m	6.20 mN/m
AFPCSMs	33.10 mN/m	6.18 mN/m	1.44 mN/m

Source: Author's contribution.

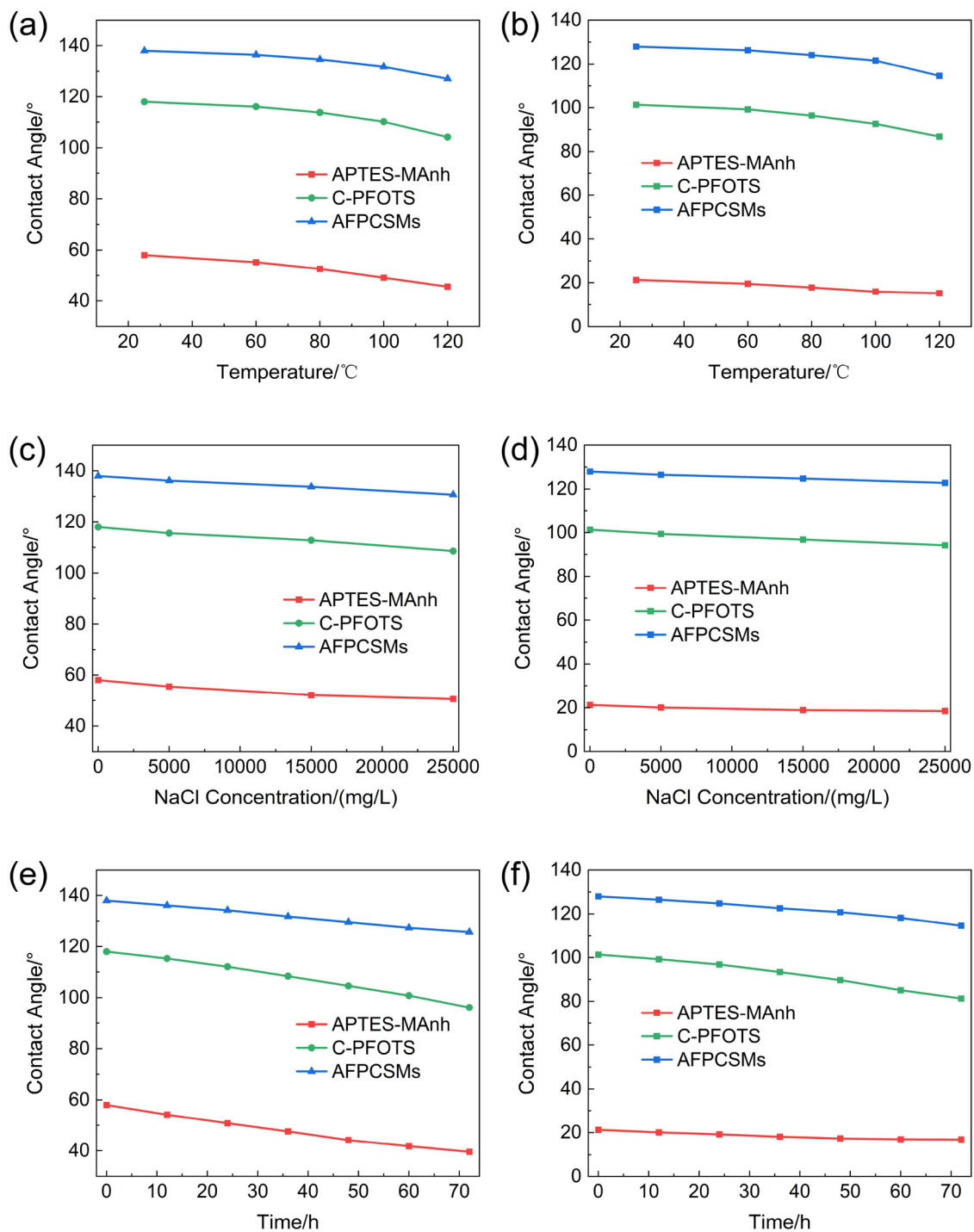


Figure 10. Stability test results of different materials. (a) Thermal stability–contact angle with water, (b) thermal stability–contact angle with *n*-hexadecane, (c) salt resistance–contact angle with water, (d) salt resistance–Contact angle with *n*-hexadecane, (e) durability–contact angle with water, and (f) durability–contact angle with *n*-hexadecane.

Source: Author's contribution.

C–N bonds and amide bond instability at elevated temperatures. Figure 10(b) shows *n*-hexadecane contact angle retention rate decreasing to 71.4%, further confirming insufficient thermal stability. C-PFOTS exhibited good thermal stability in Figure 10(a and b), maintaining 88.3 and 85.7% retention rates for water and *n*-hexadecane contact angles, respectively, after 120°C treatment, reflecting high-temperature stability characteristics of Si–C and C–F bonds [28]. AFPCSMs performed optimally at all test temperatures, maintaining 92.1% water contact angle and 89.5% *n*-hexadecane contact angle retention after 120°C treatment, where dual-shell structure thermal protection mechanisms effectively delayed functional group thermal decomposition processes.

Salt resistance testing results indicated varying degrees of impact from increased salt ion concentrations on material wettability performance. Figure 10(c) shows that under 25,000 mg/L high-salinity conditions, APTES-MANh exhibited relatively weak salt resistance with 87.2% water contact angle retention rate, indicating salt ion damage to its surface modification layer. Figure 10(d) shows *n*-hexadecane contact angle retention rate of 86.9%, similar to water contact angle performance. C-PFOTS demonstrated good salt stability in Figure 10(c and d), achieving 92.0 and 93.0% retention rates, respectively, where fluorinated surface chemical inertness effectively resisted salt ion corrosion. AFPCSMs exhibited exceptional salt resistance in Figure 10(c

and d), maintaining high retention rates of 94.7 and 95.9% even under maximum salt concentrations, where dual-shell structure barrier effects against salt ion penetration and fluorinated polymer corrosion resistance constitute key factors for excellent salt resistance performance.

Durability testing through 72-h continuous waterflooding erosion assessed long-term service stability. Figure 10(e) shows APTES-MANh exhibited obvious performance degradation under mechanical erosion, with water contact angles decreasing from 58.0° to 39.6°, achieving only 68.3% retention rate, closely related to its relatively weak surface anchoring capability. C-PFOTS demonstrated moderate durability performance with 81.4% water contact angle retention rate after 72 h, where monolayer structures face gradual detachment risks under long-term erosion. AFPCSMs exhibited excellent durability with water contact angles decreasing only from 138.0° to 125.7°, achieving 91.1% retention rate.

Figure 10(f) *n*-hexadecane contact angle durability testing further validated oleophobic performance stability. APTES-MANh *n*-hexadecane contact angles decreased from 21.3° to 16.8°; due to poor initial oleophobic performance, this decrease primarily reflects overall surface property changes. C-PFOTS *n*-hexadecane contact angles decreased from 101.3° to 81.3° with 80.2% retention rate, maintaining certain oleophobic characteristics after 72 h. AFPCSMs *n*-hexadecane contact angles decreased only from 128.0° to 114.6° with 89.4% retention rate, maintaining excellent

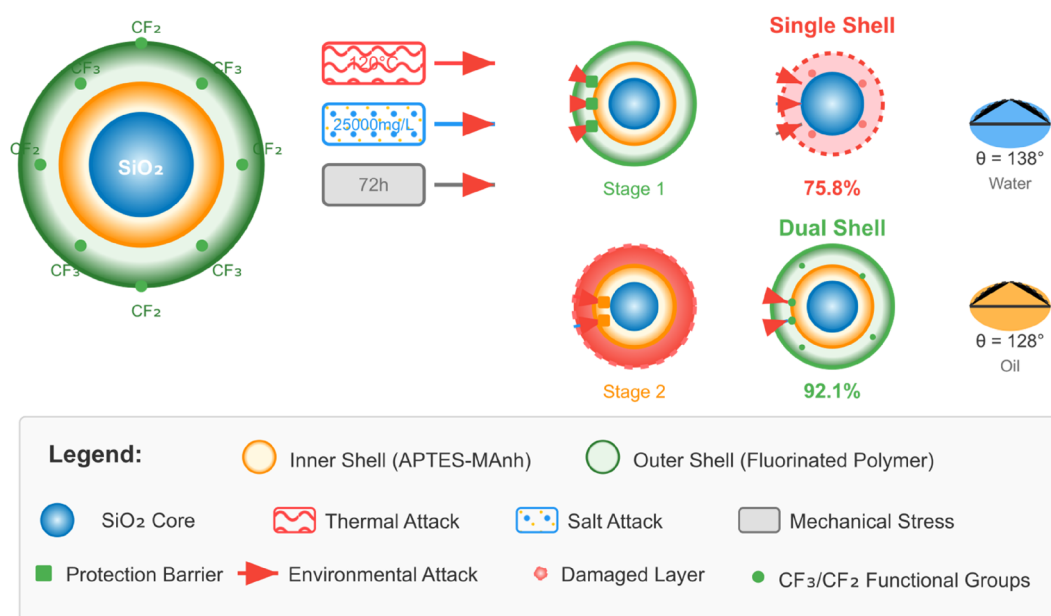


Figure 11. Analysis of stability mechanism.

Source: Author's contribution.

oleophobic performance throughout the test period. Multiple anchoring mechanisms and polymer chain entanglement effects in dual-shell structures provided exceptional mechanical stability [29].

Comprehensive analysis of Figure 10 indicates stability ranking: AFPCSMs > C-PFOTS > APTES-MAnh. Quantitative analysis shows that AFPCSMs achieved average retention rates exceeding 90% across three stability dimensions, while APTES-MAnh and C-PFOTS achieved 75.8 and 85.2%, respectively. As shown in Figure 11, AFPCSMs' excellent stability primarily stems from: (1) multi-layer protection mechanisms provided by dual-shell structures, where outer polymer layers effectively shield direct environmental impact on inner layers [30], (2) chemical inertness and low surface energy characteristics of fluorinated polymers, enhancing material anti-corrosion capabilities [31], (3) enhanced overall stability through inner-outer layer synergistic effects, delaying overall material failure through stratified decomposition mechanisms.

These results validated significant advantages of dual-shell design in improving material environmental adaptability and long-term stability. Under typical reservoir conditions (temperature 60–120°C, salinity 5,000–25,000 mg/L), AFPCSMs maintains functional stability exceeding 90% for extended periods.

3.3.3 Displacement performance evaluation

Displacement performance evaluation results revealed significant performance differences among three

nanomaterials in fluid mechanical characteristics and recovery enhancement, directly reflecting technical advantages and limitations of different surface modification strategies. Through comprehensive analysis of pressure response curves in Figure 12(a) and recovery-time curves in Figure 12(b), the influence patterns of wettability modification on fluid flow mechanisms in porous media can be thoroughly understood.

Figure 12(a) demonstrates pressure response differences among three materials during displacement processes. In the linear pressure increase segment, AFPCSMs exhibited optimal fluid mechanical characteristics with pressure increase rates of only 0.85 MPa/PV (pressure buildup per PV injected) during the initial injection phase, significantly lower than C-PFOTS (1.16 MPa/PV) and APTES-MAnh (0.99 MPa/PV), representing reductions of 26.7 and 14.1%, respectively. This parameter reflects the flow resistance characteristics in porous media during chemical flooding. APTES-MAnh exhibited sustained high-pressure characteristics throughout displacement processes, ultimately reaching 6.10 MPa, while C-PFOTS and AFPCSMs stabilized at 2.67 and 2.23 MPa, respectively. AFPCSMs' low-pressure response not only favors reduced operational costs but importantly minimizes potential reservoir damage, creating favorable conditions for economic development of low-permeability reservoirs.

Recovery-time curves in Figure 12(b) clearly demonstrate chemical flooding enhancement mechanisms. During baseline waterflooding stages (first 5 h), recovery curves for three materials highly overlapped, achieving 35.89% (APTES-MAnh), 36.05% (C-PFOTS), and 35.47% (AFPCSMs), respectively, establishing unified baselines for subsequent

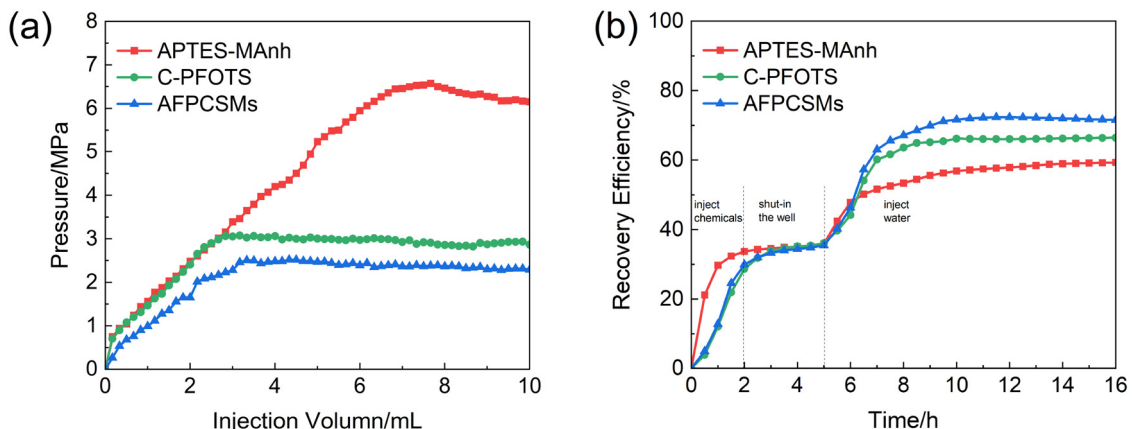
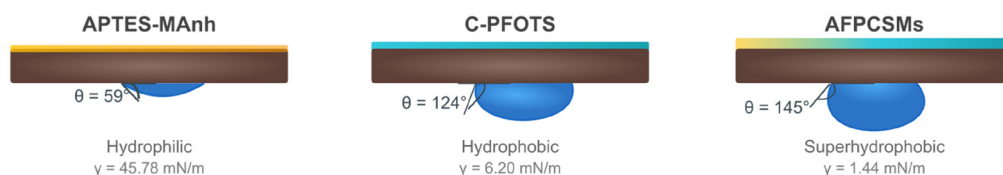


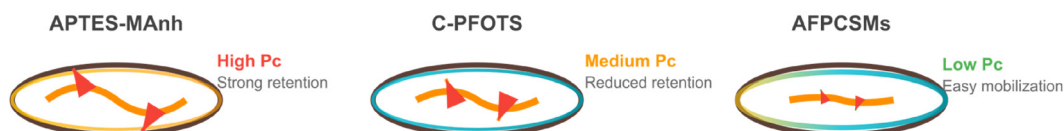
Figure 12. Evaluation of displacement performance for different materials: (a) Graph of the relationship between displacement volume and pressure and (b) relationship between displacement time and oil recovery efficiency.

Source: Author's contribution.

Contact Angle and Wetting State



Capillary Pressure in Pore Throats



Oil Mobilization and Flow Pattern

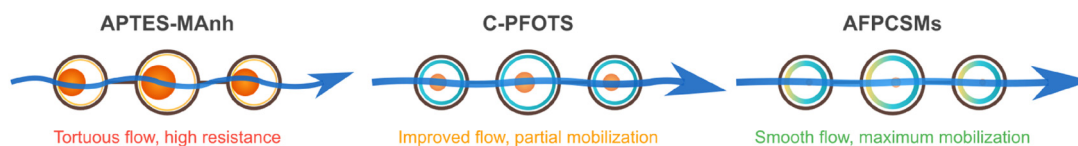


Figure 13. Schematic diagram of enhanced oil recovery mechanisms.

Source: Author's contribution.

comparisons. Following chemical injection, material performance differences significantly diverged. AFPCSMs demonstrated optimal chemical flooding effects with final recovery reaching 71.52%, chemical flooding net increase of 36.05 percentage points, and relative enhancement of 101.6%. C-PFOTS achieved final recovery of 66.44% with net increase of 30.39 percentage points and relative enhancement of 84.3%. APTES-MANh showed limited enhancement with final recovery of 59.33%, net increase of 23.44 percentage points, and relative enhancement of 65.3%. These results indicate dual-shell design possesses significant technical advantages in residual oil mobilization.

Comprehensive analysis of Figure 12(a) and (b) data shows AFPCSMs achieved ideal low pressure-high recovery combinations, obtaining maximum recovery while maintaining lowest displacement pressures, reflecting dual-shell structure technical advancement. In contrast, APTES-MANh exhibited unfavorable high pressure-low recovery combinations, indicating surface modifications increased flow resistance without corresponding recovery enhancement. C-PFOTS achieved relative balance between extremes, but overall performance remained significantly below AFPCSMs. From engineering application perspectives, AFPCSMs' pressure-recovery relationship proved most ideal, enabling efficient hydrocarbon extraction while controlling development costs and reservoir damage risks.

From microscopic displacement mechanism analysis, performance differences among materials primarily stem from varying degrees and mechanisms of wettability modification, as illustrated in Figure 13. AFPCSMs' ultra-low surface energy interfaces (1.44 mN/m) formed through dual-shell structures significantly reduced oil-water interfacial tension, where amphiphobic neutral wetting effects effectively reduced capillary retention phenomena while avoiding channeling problems caused by wettability heterogeneity [32]. Kinetic analysis from Figure 12(b) shows AFPCSMs achieved 11.5%/h recovery increase rate during initial chemical flooding phases (5–8 h), significantly exceeding other materials, indicating rapid wettability modification effectiveness. C-PFOTS single-shell fluorination modification provides effective wettability control but with relatively limited functional group density and surface coverage uniformity. APTES-MANh's limited hydrophobic capability only partially improves capillary retention effects, with high pressure responses reflecting technical limitations of surface modification strategies.

Quantitative comparisons indicate AFPCSMs performed optimally across two key displacement performance dimensions: lowest pressure gradient (0.85 MPa/PV) and highest chemical flooding relative enhancement (101.6%). This comprehensive advantage validates dual-shell design concept correctness, demonstrating that inner-outer layer

synergistic effects achieve maximum wettability modification effectiveness. Compared to conventional single-shell modification strategies, dual-shell structures not only provide higher functional group densities and more stable surface modification effects but also achieve significant fluid mechanical performance improvements through optimized surface microstructures.

From microscopic displacement mechanism perspective, the enhanced oil recovery performance of AFPCSMs can be attributed to three synergistic effects, as illustrated in Figure 13: (1) **Wettability alteration** – the ultra-low surface energy interface (1.44 mN/m) formed by the fluorinated outer shell transforms rock surfaces from strongly water-wet to intermediate-wet state, fundamentally converting capillary forces from oil-trapping to oil-releasing mode and enabling spontaneous mobilization of residual oil in pore corners; (2) **Interfacial tension reduction** – AFPCSMs adsorption at oil–water interfaces reduces interfacial tension, decreasing the capillary number threshold for oil droplet mobilization and promoting deformation and passage of trapped oil ganglia through narrow pore throats; (3) **Disjoining pressure enhancement** – the amphiphobic nanoparticle-modified surfaces create stable thin water films between oil droplets and rock surfaces, generating positive disjoining pressure that facilitates oil detachment from pore walls. These three mechanisms operate synergistically: wettability alteration reduces capillary retention forces, interfacial tension reduction enhances oil droplet mobility, and disjoining pressure modification promotes oil-rock separation, collectively enabling efficient mobilization of capillary-trapped residual oil that remains inaccessible to conventional waterflooding. The displacement performance evaluation results provide reliable technical support for industrial applications of precision reservoir wettability control technologies in challenging low-permeability formations.

4. Conclusion

This study developed dual-shell AFPCSMs for enhanced oil recovery in tight oil reservoirs. The main conclusions are as follows:

- (1) The dual-shell architecture was successfully constructed with silica cores, APTES-MANh inner shells, and TFEMA-DFHMA copolymer outer shells. FTIR, XPS, and TGA characterization confirmed the chemical integrity of each layer, with surface fluorine content reaching 15 at%.
- (2) AFPCSMs exhibited superior amphiphobic properties (water contact angle 145.3°, *n*-hexadecane contact angle

132.6°) and ultra-low surface free energy (1.44 mN/m, 95.7% reduction), significantly outperforming single-shell materials.

- (3) Excellent stability was demonstrated under reservoir conditions: 92.1% retention at 120°C, 94.7% under 25,000 mg/L salinity, and 91.1% after 72-h waterflooding.
- (4) Core flooding experiments achieved 71.52% oil recovery with 36.05 percentage points net increase (101.6% relative enhancement) and lowest pressure gradient (0.85 MPa/PV).

The dual-shell design provides an effective approach for precision wettability control in low-permeability reservoirs. Future work will address cost optimization, long-term field validation, and compatibility with oilfield chemicals to advance this technology toward practical applications.

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Author contributions

Guojie Sui: Conceptualization, Methodology, Investigation, Writing – original draft. Hai Lin: Investigation, Data curation. Huan Liu: Investigation, Formal analysis. Tingsong Xiong: Investigation, Validation. Shiduo Liu: Resources, Supervision. Shijun Chen: Conceptualization, Supervision, Writing – review & editing, Project administration.

Conflict of interest statement

Authors state no conflict of interest.

Data availability statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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