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Invited review

Research progress and prospects of utilizing carbon-based nanomaterials in enhanced oil recovery

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Abstract:
Carbon-based nanomaterials have received heightened global interest by petroleum researchers because of their abundant stocks of necessary raw materials, ease of size control, readiness for modification, and high stability. In light of the practical demand for oil development, this study reviews the recent progress in the research of enhancing oil recovery using carbon-based nanomaterials of various dimensions, including carbon dots, carbon nanotubes, carbon nanofibers, and graphene and its derivatives. Moreover, the study elaborates on the application of these materials in high-efficiency oil displacement, profile control and water shutoff, as well as the fracturing process. The related challenges and solutions in practical oil exploration and development are analyzed, and the application prospects of these materials in future oil reservoirs and oilfields are predicted. This review provides valuable theoretical and experimental references for the large-scale application of carbon-based nanomaterials.

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1. Introduction

According to the Organization of the Petroleum Exporting Countries (OPEC) forecasts, global energy demand will grow by 24% from this year to 2050 (OPEC, 2024). The available resources of oil, as the main source of energy, are gradually decreasing while the demand is steadily on the rise. As the second largest oil and gas consumer, China must tackle the challenges of the deep exploitation of conventional resources and the efficient exploitation of unconventional resources. The development of oil exploitation methods that are effective in enhanced oil recovery (EOR) is crucial for national energy security.

Nanotechnology, an idea first proposed by Richard Feynman in 1959, relates to the manufacture of materials on the atomic or molecular scales and the study of materials at the nanoscale, that is, in the 1-100 nm range (Hulla et al., 2015; Liu et al., 2016). By 2016, more than 60 countries had launched national nanotechnology programs and a number of cutting-edge problems have been solved through this technology, which has therefore become a focus of petroleum research in recent years. A typical application of nanotechnology in the petroleum industry is the incorporation of nanoscale materials or those with nano-properties into the oil development stages (Liu et al., 2018). Nanomaterials are those with at least one dimension of 1-100 nm in three-dimensional space. They exhibit distinctive size, interface, quantum effect, and mechanical properties that differ significantly from those of conventional chemicals because of their large surface area, high surface/interface activity, small size, and the ability to focus on interface control, offering great application potential in EOR.

Carbon-based nanomaterials are carbon-bearing materials whose disperse phase has at least one dimension that is less

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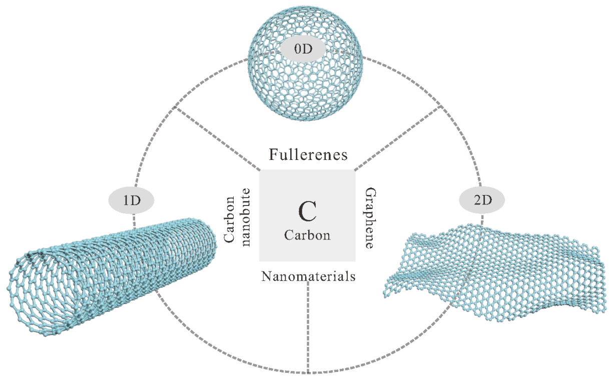


Fig. 1. Classification of carbon-based nanomaterials in different dimensions (modified from Choudhary et al. (2024)).

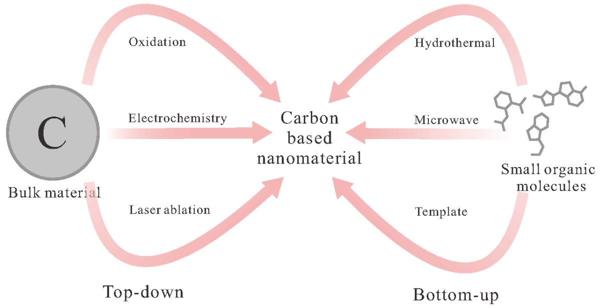


Fig. 2. Two different approaches to the synthesis of carbon-based nanomaterials (modified from Choudhary et al. (2024)).

than 100 nm in size. Due to the abundant carbon resources, low toxicity, high stability, simple size control, and readiness for surface modification and doping, carbon-based nanomaterials have found applications as biosensors, transparent electrodes, reinforcing materials, and physical carriers in the electronics, aeronautics, medical care, and environmental fields, and also have been considered as one of the most promising new subfields of nanotechnology for high-quality petroleum development. Carbon, as the fourth most prevalent element in the universe, is an important cornerstone of energy and materials in human society. The carbon atom, with four electrons in its outermost shell, can combine with itself or other elements. According to the different arrangement of sp^2 and sp^3 hybrid carbon atoms, carbon-based nanomaterials with different forms can be constructed, including zero-dimensional (0D) ones such as spheroid or cage-like carbon dots (CDs) and fullerene, one-dimensional (1D) ones such as hollow tubular carbon nanotubes (CNTs) and carbon nanofibers (CNFs), and two-dimensional (2D) ones such as lamellar graphene and its derivatives (Hajiabadi et al., 2020; Cabral et al., 2024). This shape diversity endows the materials with high stability, large surface area, and high conductivity. This review discusses the raw material sources, synthesis paths, modification methods, and application effects of different dimensional carbon-based nanomaterials from the aspects of high-efficiency oil displacement, profile control and water shutoff, and fracturing process, then examines the prospects of their application potential in EOR.

2. General description of carbon-based nanomaterials

On the basis of growth direction, carbon-based nanomaterials can be classified into four categories: 0D, 1D, 2D, 3D. According to their different dimensional structure, they also have different shapes, which results in their outstanding properties. For instance, CDs, which are 0D spherical particles with confinement in all three dimensions, exhibit uniform size and high stability. In contrast, CNTs with high aspect ratios, classified as 1D hollow tube structure materials, are known for their excellent conductivity and superior mechanical properties. Graphene, a 2D lamellar material, stands out for its large specific surface area and strong interfacial activity (Choudhary et al., 2024). The particle size or shape also affects the flow path of carbon-based nanomaterials in heterogeneous reservoirs. The nano-size effect of these materials enables them to enter finer pores, affecting their movement in rocks. The interaction of carbon-based nanomaterials with water, oil and minerals can be adjusted by introducing hydroxyl, carboxyl, amino and other groups on their surface through functionalization, so that the rock surface becomes hydrophilic or hydrophobic, which will also affect their movement and retention in rock pores. Compared with 1D and 2D materials, the size advantage of 0D material makes entry easier to the formation pores, which is more conducive to EOR in low-permeability reservoirs. Compared with 0D materials, the large surface area and outstanding mechanical properties of 1D and 2D materials make them more suitable for EOR in medium- and high-permeability reservoirs. Considering that 3D nanomaterials have been rarely included in studies on petroleum development, this review will focus on the classification, preparation and modification of carbon-based nanomaterials in the 0D, 1D and 2D categories (Fig. 1).

2.1 Preparation and modification of carbon-based nanomaterials

Carbon-based nanomaterials are prepared either in a “top-down” or “bottom-up” manner (Fig. 2). The former involves the exfoliation of bulk carbon materials, such as carbon black and graphite, into smaller nanoparticles via laser ablation, electrochemistry, chemical oxidation, or arc discharge, while the latter involves the carbonization of carbon-bearing organic substances as precursors, followed by their transformation into nanomaterials via hydrothermal/solvothermal, template, or microwave-assisted treatments (Namakka et al., 2023). For example, in the fabrication of CNTs via arc discharge, a high-temperature arc is generated between two graphite electrodes placed in close proximity in a helium atmosphere, so that the anodic graphite electrode evaporates and deposits on the cathode surface. In this process, material growth is notably affected by power and air pressure. Alternatively, nanotubes can be ablated via laser vaporization in a high-temperature inert gas atmosphere. Chemical vapor deposition (CVD) is another commonly used synthesis method, which uses methane, ethanol and acetylene as the gas and Fe, Ni, Co, Pd, Pt, Au, Mn, and their compounds as the catalyst. On the basis of the reaction conditions, CVD can be categorized as thermal CVD, microwave plasma CVD, plasma-enhanced CVD, low-pressure CVD, and floatation-catalyzed CVD (Zhang et al., 2024). Moreover, CVD is widely used for growing mono- or few-layer graphene to catalyze the growth of graphene by having a similar lattice of metal elements to the structure of graphene. Combustion and other chemical processes are also employed, wherein benzene or toluene vapor is combusted together with oxygen in a given proportion under low pressure to form fullerene-containing soot, which is then purified into fullerene.

For high-temperature, high-pressure, high-salinity reservoirs, the surface of carbon-based nanomaterials needs to be modified to ensure sufficient temperature resistance, salt resistance, and dispersion stability. This can be achieved by introducing surface defects and functional groups via heteroatom doping and surface passivation to precisely control the structural and physiochemical properties and ensure the optimal performance of these materials. Heteroatom doping is the use of the nonmetallic elements N, S, P, and B to replace sp^2/sp^3 carbon atoms to alter the electron structure, chemical composition, and properties of materials. Alternatively, the metallic elements Mn, Cu, Fe, and Zn, and rare earth metals can be used for this purpose, although this approach has not been extensively reported. Surface passivation is achieved via covalent or noncovalent modification. Covalent modification means forming covalent bonds between a material and a modifier via the sharing of outer electrons, which introduces new functional groups and creates a new conjugated system, thus altering the properties of the targeted material. Such reactions include amide coupling, copolymerization, sulfonation, esterification, silylanization, etc. Nguyen et al. (2020) observed that modifying TiO_2 with silane couplers inhibited particle agglomeration and yielded its satisfactory stability. Among the variety of groups, the effect of sulfonic acid group on improving temperature and salt tolerance has proved better. Wu et al. (2023b) found that compared with hydroxy-modified (H-CDs) and amine-modified carbon dots (A-CDs), 0.2 wt% benzened sulfonated-modified carbon dots (BS-CDs) could withstand being placed in an oven at 100 °C for 7 days under the condition of 14×10^4 mg/L salinity, while H-CDs and A-CDs had poor temperature and salt resistance (< 80 °C, 5×10^4 mg/L salinity). Furthermore, the application of BS-CDs in core flooding tests could achieve an EOR 27.88% higher than that of water flooding, outperforming traditional nanomaterials. Noncovalent modification can achieve surface modification by combining functionalized small molecules via $\pi - \pi$ stacking, electrostatic interaction, and the synergistic interaction of multiple forces, whereby the surfactants and polymer molecules are adsorbed onto the sidewalls of CNTs and they introduce a charge to the nanotube surface, thus preventing the aggregation of nanotubes by virtue of charge repulsion (Zhang et al., 2022).

2.2 Zero-dimensional carbon-based nanomaterials

These nanomaterials are dotted or spherical nanoparticles with sizes varying from 1 to 100 nm in all three dimensions. Common examples include CDs and fullerene. Fullerene was reported to be a remarkable photosensitizer with very high quantum yields ($\varphi \approx 1$), which could enhance photoelectric efficiency by increasing light absorption and charge transfer capacity (Kumar et al., 2018). CDs feature vast potential as a high-resolution bioimaging contrast medium because of their unique optical properties, providing a basis for the real-time monitoring of biological processes (Das et al., 2024).

2.2.1 Fullerene

Fullerene merits distinction for being the first ever carbon-based nanomaterial to be studied. Discovered by Kroto, fullerene has a hollow cage-like structure constructed by 12 pentagons and multiple hexagons of sp^2-bonded carbon atoms (Kroto et al., 1985). Depending on the total number of carbon atoms, fullerene can exist in different forms, such as C_{60}, C_{70}, C_{76}, C_{82}, or C_{84}.

Fullerene is typically synthesized via laser, arc, and combustion. Gerhardt et al. (1987) detected free-state fullerene from the combustion product of hydrocarbon. Krätschmer et al. (1990) synthesized a large amount of fullerene for the first time by heating two contacted graphite rods in an inert gas atmosphere. Thereafter, Howard et al. (1991) noted that the combustion product of a mixture of benzene vapor and oxygen at low pressure contained fullerene, and that a continuous supply of the mixture gas could result in continuous synthesis of this material. Additionally, replacing carbon atoms in fullerene cages with atoms like nitrogen or fluorine can produce heterofullerenes, while grafting functional groups onto the carbon cages forms exofullerenes. Most lanthanides and transition metals can be embedded as a cluster into carbon cages to form embedded fullerenes (Gillan et al., 1992; Wang et al., 2000). The encapsulation of fullerene with hydrophilic polymers or the modification of the surface of carbon cages with water-soluble groups can result in increased water solubility. For example, Kop et al. (2020) encapsulated fullerene with pyridine as the solvent and fructose, branched-chain starch, and cholesterol as the surfactants, to achieve a form of fullerene with higher chemical stability and lower biotoxicity.

2.2.2 Carbon dots

CDs were first discovered by Xu et al. (2004) while purifying single-walled nanotubes via electrophoresis and formally named by Sun et al. (2006). According to carbon nuclei composition, CDs can be classified into carbon quantum dots (CQDs), graphene quantum dots (GQDs), and carbon polymer dots (CPDs), as seen in Fig. 3 (Chen et al., 2021; Qureshi et al., 2024). CQDs are spherical or quasispherical nanoparticles with a diameter of less than 10 nm and comprising amorphous or crystalline sp^2/sp^3 carbon clusters. GQDs are nanoscale particles with one or more layers, which are synthesized by reducing graphene to a horizontal dimension of about 20 nm. GQDs have a surface structure similar to that of CQDs, and their internal carbon nuclei also have the same lattice structure as those of graphene. This affords GQDs a larger specific surface area, higher conductivity, and superior mechanical property in addition to the essential qualities of CQDs (Liu et al., 2020). CPDs are core-shell structures comprising qua-

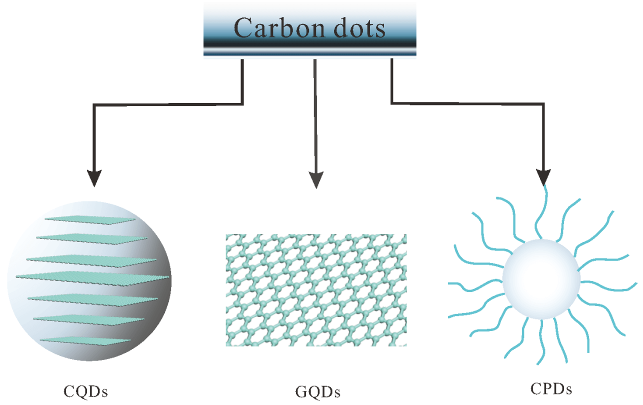


Fig. 3. The three types of CDs: CQDs, GQDs and CPDs.

sicrystalline carbon nuclei of tiny carbon clusters as the core and hydrophilic groups or polymer chains as the shell (Zhu et al., 2012). This makes them more stable, biocompatible and conducive to modification and functionalization in comparison with CQDs.

The surface of CDs usually contains abundant oxygen- and nitrogen-bearing groups such as hydroxyl, amino, and carboxyl, ensuring satisfactory water solubility and highly controllable surface chemical activity. Nitrogen doping can notably expedite the electron transfer rate in molecules and thus generate brighter fluorescence without considerably increasing the size of CDs (Wang et al., 2012). Phosphorus atoms, with their high electron-supply capacity, can increase electron transfer capacity by providing new active sites for CDs (Zhou et al., 2014). Sun et al. (2006) observed the pronounced fluorescence properties of CDs upon passivation of the surface of carbon particles with polyethylene glycol. Pappalardo et al. (2020) synthesized PDA-CDs via microwave-assisted pyrolysis using polydopamine (PDA) as the passivation agent to obtain an increased quantum yield. The addition of the polymer molecules also contributed to the stability of the CDs. Modified CDs usually exhibit better optical and electronic properties, higher biocompatibility and water solubility, and more stable physiochemical behavior.

2.3 One-dimensional carbon-based nanomaterials

One-dimensional nanomaterials are nanoscale materials with particle sizes ranging from 1 to 100 nm in two dimensions but larger sizes in the third dimension. These generally include nanowires, nanotubes and nanorods. Currently, CNTs and CNFs are the primarily considered 1D carbon-based nanomaterials. Highly conductive CNTs help increase the energy density and power density of supercapacitors. Moreover, due to their extremely low weight and high strength, CNFs are widely used in the structural parts of aircraft and spacecraft to increase their strength and rigidity.

2.3.1 Carbon nanotubes

CNTs comprise one or more sheets of six-membered graphene rings rolled into nanoscale hollow cylinders, in which the carbon atoms are usually sp^2-bonded. Iijima (1991) synthesized a CNT structure via arc discharge evaporation using a current of 100 A. Guo et al. (1995) employed the laser process to fabricate high-performance single-walled CNTs. On the basis of the number of graphene sheets, CNTs can be categorized as single-walled CNTs (SWCNTs), double-walled CNTs (DWCNTs), and multiwalled CNTs (MWCNTs), where the structure of resultant CNTs varies as per the manner of rolling.

CNTs are distinctly anisotropic materials in view of their large aspect ratio and extremely fine hollow fibers. They possess extraordinary mechanical properties: Results of laboratory experiments demonstrated that ideally structured SWCNTs can have a Young's modulus of 1.2 TPa and a tensile strength of two orders of magnitude higher than that of steel (Wang et al., 2005). The exceptionally strong bonding between atoms in CNTs also ensures high thermal stability in addition to their remarkable thermal conductivity. Besides, CNTs exhibit very high electrical conductivity; the conductivity of SWCNTs is on the order of 10^6 S/m, and that of MWCNTs is on the order of 10^5 S/m at 300 K (Thess et al., 1996; Ando et al., 1999). However, the high hydrophobicity of CNTs results in their easy aggregation, which can be mitigated via functionalization to increase their solubility. Gong et al. (2009) employed chemical vapor deposition to successfully fabricate an N-doped CNT array by introducing ammonia into CNTs and reported notable improvement in material performance. Song et al. (2019) modified CNTs using reactive red 195 (RR195) $\pi-\pi$ conjugated molecules via ultrasonication or ball milling and achieved high solubility and high stability in the aqueous phase. Mozaffarinasab and Jamshidi (2024) treated MWCNTs with mixed acid (nitric acid and sulfuric acid), followed by surface modification with 3-glycidyloxypropyltriethoxysilane, which yielded increased stability and compressive strength of the CNTs.

2.3.2 Carbon nanofibers

CNFs are materials comprising multiple layers of graphene or graphite arranged in various forms (e.g., parallel, rolled) into tubes or fibers with a considerable length and a diameter at the nanoscale ranging from a few to tens of nanometers. The high tensile strength (up to 7 GPa), low density (1.75-2.00 g/cm^3), and exceptional electrical and thermal conductivities of CNFs account for their frequent presence in composites and catalysts. Although CNFs cannot stably exist in the air at high temperatures because of their lack of oxidation resistance, they are essentially stable in various chemical environments (Ding et al., 2018).

Currently, CNFs are usually prepared via electrospinning and vapor deposition. A variety of precursors, such as polycrylonitrile, cellulose, polyethylene, and metal-organic frameworks, have been used to prepare CNFs. Since these CNFs are typically surface-coated with a layer of microcrystalline graphite, their surfaces are chemically inert and exhibit low energy. Consequently, surface modification becomes essential to improve the adhesion and wettability of these materials. Athulya et al. (2022) coated CNFs with an acrylate-derived polymer with aromatic side chains, and found that the tensile strength and tensile modulus of the modified CNFs increased by 23.7% and 8%, respectively, and remained 20% and 7% after being heated to 600 °C. Guo et al. (2020) prepared Fe/Ni-doped CNTs via electrospinning and high-temperature heating. Electrochemical measurements indicated that these modified CNFs had abundant pores, and they could be prepared at low cost. Belaustegui et al. (2018) fabricated doped CNFs with high nitrogen content. This was achieved by introducing modified graphene oxide pretreated with sodium nitrate and potassium permanganate into an electrospinning solution and carbonizing it at a temperature less than 500 °C. The authors observed that the N-doping procedure resulted in higher electrical conductivity.

2.4 Two-dimensional carbon-based nanomaterials

Two-dimensional carbon-based nanomaterials constitute thin layers of materials comprising carbon atoms, whose nanoscale is limited to one dimension and that are a few atom layers thick at most. Graphene and its derivatives are ideal 2D carbon-based nanomaterials with an ultra-large specific surface area and remarkable surface activity. Due to its extremely high sensitivity, graphene is widely used in the manufacture of sensors for the detection of biomolecules, heavy metals, and chemical pollutants. Additionally, graphene oxide (GO) can also be employed as a reinforcing material to enhance the mechanical properties and conductivity of plastics and metals.

2.4.1 Graphene

Graphene is a 2D honeycomb crystal structure of sp^2 hybridized carbon atoms tightly packed into a single atomic layer. Novoselov et al. (2004) synthesized graphene via mechanical exfoliation, which won them the Nobel Prize for Physics in 2010 and laid the groundwork for subsequent research on graphene. This process involves the exfoliation of graphite using adhesive tape until single sheets of graphene are obtained. In contrast, liquid-phase exfoliation opens the gaps between graphite layers via small molecule intercalation or oxidation to result in single-layer structures. This method is considered satisfactory for mass production but might introduce surface defects, compromising material performance (Stankovich et al., 2007).

Graphene can also serve as the basic unit of fullerene, CNTs, and graphite. Its unique one-atom-thick layer and electronic structure afford it high strength, satisfactory thermal conductivity, as well as an ultra-large specific surface area. The carbon layer can also introduce special functional groups (such as $-NH_2$, $-COOH$, $-OH$, and $-C=O$) for surface modification, thereby enhancing the interfacial interaction between graphene and other substances. The hydroxyl groups at the top of graphene can react with the ethers or amides and be functionalized. The adsorption of polymer molecules onto graphene can also increase its dispersibility and stability in solvents via covalent functionalization (Perala et al., 2024). Moreover, doping with metallic atoms can generate active sites. Achra et al. (2021) noticed that doping graphite sheets with elemental Ru decreased the material's resistance by 18% and increased its electrical conductivity. Aftab et al. (2017) demonstrated that at high temperature and pressure, using graphite nanosheets in water-based drilling mud enhanced their rheological properties more effectively than using them in other additives, probably due to the lower friction between the nanosheets and fluids.

2.4.2 Graphene oxide

GO is an important derivative of graphene, in which graphite is oxidized so that some of the carbon atoms are transformed from an sp^2 to an sp^3 hybridization state. Although the conjugated system of graphene is retained on the surface, the integrity is damaged to an extent, affording GO a physiochemistry different from that of graphene.

Compared with graphene, the surface of GO contains numerous oxygen-bearing functional groups such as carboxyl, carbonyl, and epoxied, which provide abundant reactive sites for the functionalization of functional groups to facilitate isocyanation, carboxylation, epoxy ring opening, and diazotization. Additionally, due to the presence of oxygen-containing functional groups at the edges, the GO surface can also be functionalized via hydrogen bonding and electrostatic interactions. These groups are satisfyingly hydrophilic and can be evenly dispersed in water to form a stable aqueous solution. Mangadlao et al. (2015) demonstrated that GO as an additive to cement enhances its compression strength, flexural rigidity, and ductility. Haruna et al. (2024) prepared a nanofluid by utilizing the bonding effect between GO and hydrolyzed polyacrylamide (HPAM), and achieved excellent thermal stability. Khoramian et al. (2022) introduced sodium dodecyl benzene sulfonate (SDBS) into GO nanosheets, which generated electrostatic repulsion forces between them and prevented particle aggregation even at high salinity levels of 60,000 ppm NaCl for 2 weeks. Cao et al. (2022) prepared an innovative polyoxyethylated GO-based nanofluid (P-GO-O) via the modification of GO using octadecyl amine and polyoxyethylene, such that it had a polyoxyethylene hydrophilic side and an octadecyl hydrophobic side. Compared with GO, P-GO-O was more dispersive and exceptionally stable under high temperature and high salinity. Moreover, GO was subjected to a reduction treatment to obtain reduced GO. During this process, the oxygen-bearing groups were partly or completely removed, which notably increased the electrical conductivity of graphene.

3. Application of carbon-based nanomaterials in enhanced oil recovery

3.1 High-efficiency oil displacement

Oil displacement means the use of various technical means to maximize oilfield recovery, so that more crude oil can be extracted from the reservoir. Nanomaterials have stimulated extensive interest among researchers in this aspect, as they are sufficiently small to penetrate rock pores and fractures irrespective of pore throat size. Nanofluids are homogeneous fluids synthesized via a high dispersion of nanomaterials in aqueous media. Based on theoretical calculation and experimental study, Wasan and Nikolov (2003) observed that nanoparticles tend to exfoliate crude oil by forming a wedge-

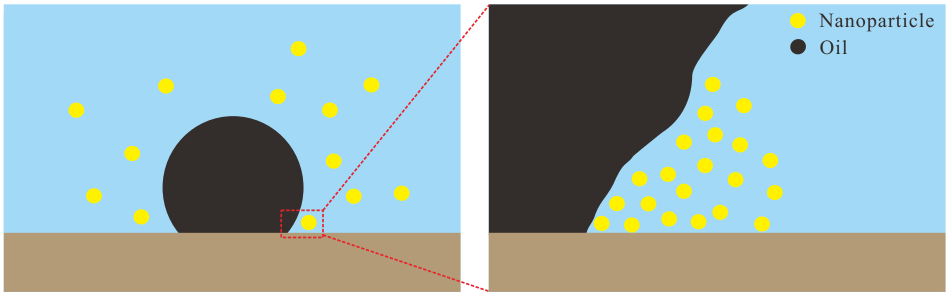


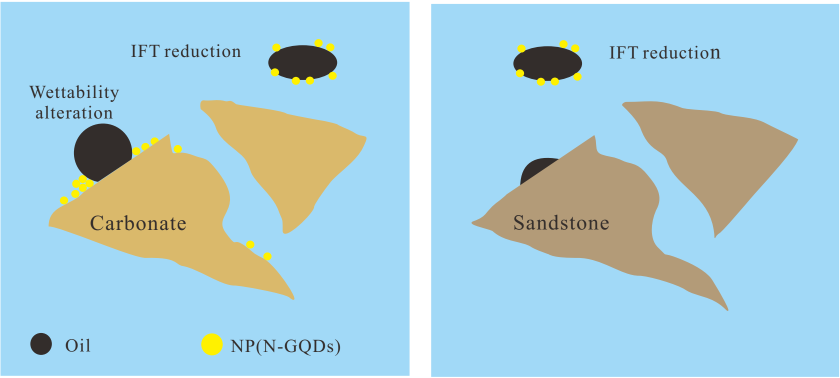
Fig. 4. Image of increasing separation pressure mechanism.

shaped structure at the oil-water-solid contact (Fig. 4). Currently, the key effective means to facilitate nanofluid flooding include decreasing oil-water interfacial tension (IFT) and altering rock wettability.

Nanomaterials such as SiO_2 and metal oxides can achieve oil displacement to varying degrees. Ogolo et al. (2012) studied the flooding properties of an aluminum oxide nanofluid and observed that it could decrease not only IFT but also crude oil viscosity. Ebrahimi et al. (2018) observed that TiO_2, Al_2O_3, and SiO_2 nanofluids could alter rock wettability from oleophilic to hydrophilic, and 0.1 wt% of these nanofluids increased the respective crude oil recoveries by 12.38%, 15.66% and 18.27%. Apart from nanomaterials such as metal oxides and nanosilica, carbon-based nanomaterials are also favored as an ideal alternative for nanoscale flooding because of their wide availability, easy synthesis, and satisfactory stability. In terms of cost, metal oxides are synthesized by the hydrothermal/solvothermal method, which is simple but its modification process is relatively complex. The raw materials for preparing carbon dots are cheap and easy to obtain, and by-products of petroleum industry such as petroleum coke and asphalt can be used at low cost. In terms of EOR, carbon-based nanomaterials usually have higher efficiency in the process of oil and gas exploitation due to their large surface area and easy modification, especially in application scenarios that need to adjust wettability and control fluidity. Luo et al. (2016) synthesized a graphene-based Janus amphiphilic nanosheet system that was highly effective at low mass concentrations; results of core flooding experiments indicated that 0.01 wt% of the graphene-based amphiphilic nanofluid enhanced the flooding performance by three times compared with the optimal performance of traditional nanofluid flooding.

Carbon-based nanomaterials are more stable than conventional flooding media. Kanj and Kosynkin (2015) noted the stability of A-Dots under the harsh formation conditions of the Arab-D carbonate reservoir in Saudi Arabia. They observed that modified A-Dots could remain stable under a reservoir temperature of 100 °C and formation water salinity of 120,000 mg/L. High temperature and high pressure may lead to the degradation of material properties. Graphene and CNTs usually exhibit good thermal stability at high temperature; however, when the temperature exceeds a certain threshold or the pressure is too high, structural changes or desorption may occur. To maximize the application of carbon-based nanomaterials, their stability in different environments needs to be optimized, including structural optimization and surface modification. Namin et al. (2019) suggested that N-doped graphene had satisfactory stability, as it was able to remain stable for 16 months at 80 °C under high salinity conditions. The nanofluid decreased the IFT by 49.2% with a concentration of 200 mg/L, and it could also alter the core wettability from oleophilic to hydrophilic, yielding an EOR of 16.42%.

IFT is the free energy per unit surface area between two dissimilar immiscible liquids. A decrease in IFT can reduce the binding force of rock on crude oil, thereby improving oil recovery. The addition of carbon-based nanomaterials (such as graphene, CNTs, CDs) can reduce IFT to 40%-60%. Due to a number of modifiable active sites of CDs and the large surface area of CNTs and graphene, they can be effectively adsorbed on the oil-water interface. This adsorption can alter the interfacial surface energy and thus significantly reduce the IFT. Tajik et al. (2018) synthesized a functionalized silicone-graphene nanohybrid via chemical vapor deposition and experimentally demonstrated that this nanohybrid decreased the IFT by 60%, implying its enormous application potential. Wettability refers to the dispersion of liquid on the surface of reservoir rock under the action of molecules. Usually, it is manifested as water wet type, oil wet type, mixed wet type, and so on, due to the influence of different rock mineral compositions and reservoir fluid compositions. The degree of wettability change can be used to visually observe the changes in the oil-water-solid three-phase contact angle in nanofluids using a contact angle meter, and the change in the micro-wettability of core surface before and after nanoparticle adsorption can be measured by atomic force microscopy. The reservoir rocks are mainly sandstone and carbonate rocks. Sandstones are mainly composed of quartz, which has a more hydrophilic surface, whereas carbonate rocks are composed mainly of minerals such as dolomite and calcite. Calcite usually exhibits a more hydrophilic surface, while dolomite may show a more hydrophobic surface. Carbon-based nanomaterials will produce different wetting effects on different rock surfaces due to their varying surface chemical properties and morphological structures. Since the surface of sandstone usually contains some hydrophilic functional groups, the introduction of graphene or carbon nanotubes, etc. may significantly change the wettability by altering surface polarity. The main components of carbonate rocks are easily reacted with water and acid, and carbon-based nanomaterials may change the wettability behaviors by affect-



(a) (b)

Fig. 5. Schematic illustration of EOR mechanisms in (a) carbonate core and (b) sandstone core (modified from Nasr et al. (2021)).

ing the microstructure and chemical reactivity of carbonate rock surfaces. The surface of CDs can be doped by different chemical modifications (such as the introduction of amino, carboxyl or other polar groups) to adjust their hydrophilicity or hydrophobicity. These modifications can change the wetting properties of rocks by interacting with mineral components on the rock surface, and also interact with the rock surface through electrostatic force or van der Waals force. CNTs, with their high surface energy and unique nanostructures, are able to provide a large contact area on the rock surface. When they are introduced onto the rock surface, they may alter wettability due to their special surface hydrophilicity or hydrophobicity modulation. For example, the hydrophilicity of graphene can be significantly increased when its surface is oxidized or oxygen-containing groups are introduced (e.g., carboxyl, hydroxyl, etc.). This surface chemical modification will cause graphene to enhance its hydrophilicity on certain rock surfaces, thus improving the wettability properties of rock. Nasr et al. (2021) synthesized N-doped GQDs (N-GQDs) sized 3.5-180 nm via one-step hydrothermal carbonization. Compared with water flooding, N-GQDs nanofluids with a mass fraction of 0.05% and an average particle size of 3.5 nm increased the recovery of carbonate cores by 18% and sandstone cores by 14%, respectively. The comparison showed that the N-GQDs nanofluid could alter the surface wettability of the carbonate rock and effectively decrease IFT at the same time, while it did not remarkably alter the surface wettability of sandstone (Fig. 5). The smaller the particle diameter of the nanofluid is, the better its ability to alter rock wettability and decrease IFT.

Furthermore, carbon-based nanomaterials are easy to synthesize. Wu et al. (2021) conducted extensive experiments on the synthesis and flooding efficiency of CDs. They employed an electrochemical process to synthesize high-hydrophilicity CDs (hh-CDs) with an average particle size of 2.54 ± 0.016 nm, which led to satisfactory dispersibility and stability and could considerably decrease the surface roughness of rock while altering its microwettability. The results of core flooding experiments indicated that without introducing any surfactant, 0.20 wt% hh-CDs fluid increased the core recovery by 26.38%. They then used the hydrothermal process to synthesize amino-modified CDs (am-CDs) with an average particle size of 2.6 ± 0.040 nm, and the results showed that the resultant nanofluid could be favorably adsorbed on the core surface, so that its micro-wetting characteristics changed from oil wetting to relatively uniform water wetting. This could also notably decrease the adhesion of alkanes to the surface of sandstone, so as to facilitate oil droplet peeling. Without adding any surfactant, 0.30 wt% am-CDs achieved a recovery of 54.09%, considerably outperforming that of water flooding at 30.25%, nanosilica flooding at 36.45%, and amino-free CDs flooding at 37.8% (Wu et al., 2023a). Moreover, the recovery of crude oil from reservoirs could be maximized by adjusting the surface and rheology of nanoparticles via morphology, size control and surface modification during synthesis. Soleimani et al. (2018) synthesized MWCNTs via chemical vapor deposition and conducted glass bead-filled column flooding experiments, and found that the addition of 0.3 wt% MWCNTs led to a recovery of 18.57%, which was attributed to IFT decrease and wettability alteration. Zhao et al. (2023a) synthesized novel, spherically dispersed modified carbon black (MCB) nanoparticles with an average particle size of 72.3 nm via oxidation, acyl chlorination, and activated grating of carbon black (CB). Compared with CB nanoparticles, the MCB nanoparticles were more dispersible and stable, allowing them to penetrate deeper into the formations. The MCB nanoparticles could also effectively decrease IFT and alter the surface wettability of sandstone, resulting in a 27.27% increase in final recovery.

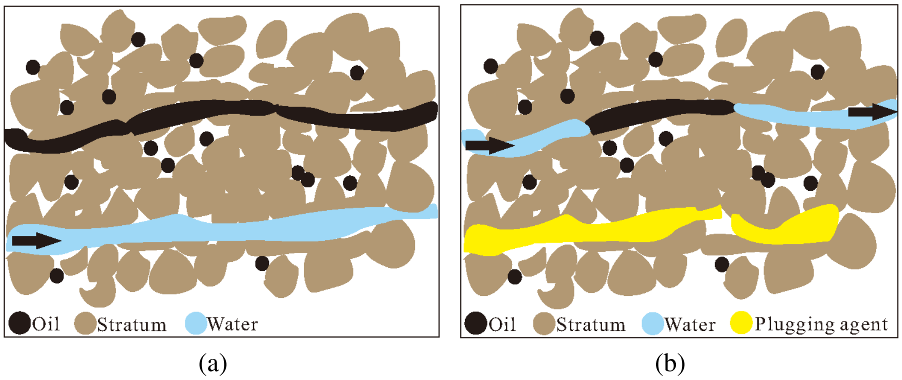
In addition to introducing chemicals into the injected water, the addition of composite flooding agents comprising two or more chemicals, such as polymers and surfactants, can increase both sweep coefficient and flooding efficiency. This is achieved by utilizing the ability of polymers to control fluidity, coupled with the ability of surfactants to considerably decrease IFT and alter wettability (Sidiq et al., 2019). However, an issue with using polymers and surfactants as chemical flooding agents for highly mineralized reservoirs is that they cannot provide the desired viscosity enhancement and solubility when exposed to high mass concentrations of Ca^{2+} and Mg^{2+}. Hence, it is crucial to obtain flooding systems that provide satisfactory viscosity enhancement while maintaining low IFT with crude oil at high salinities. Using nanomaterials as an additive can enhance the viscosity of the flooding system and reduce IFT. Maghzi et al. (2013) tested the flooding performance of a polyacrylamide (PAM) and silica nanoparticle composite system (mixture) under various mineralization levels and used glass micromodels to examine the rheological behavior of the mixture. The flooding test results indicated that 0.1 wt% silica nanofluid could retain PAM viscosity under high-mineralization conditions via PAM reduction caused by divalent cations and resulted in a 10% increase in flooding efficiency. Maurya and Mandal (2016) compared the rheological behaviors of PAM solutions with and without silica nanoparticles, and found that the introduction of 0.1 wt% SiO_2 enhanced the properties of the polymer solutions. PAM formed a 3D network structure around the silica nanoparticles and became more resistant to shear, temperature and salinity changes. Sharma et al. (2016) experimentally examined a composite system comprising silica nanoparticles, polymers and surfactants. Compared with conventional surfactant/polymer (SP) binary compound flooding, the introduction of nanoparticles resulted in more than 20% EOR because of decreased IFT and stabilized emulsions. For instance, Chen et al. (2018) synthesized an MWCNT/α-olefin sulfonate composite system using MWCNTs as the surfactant carrier and examined the flooding efficiency of the system. Compared with surfactant-only formulations, the composite system resulted in a 10.4% crude oil recovery enhancement. Moreover, MWCNTs decreased the adsorption loss of α-olefin sulfonate, as these nanotubes as α-olefin sulfonate carriers benefit the migration and dispersion of α-olefin sulfonate molecules toward the oil-water interface and also increase the injection efficiency of the flooding agent. Furthermore, Razavinezhad et al. (2022) investigated the effect of MWCNTs on SP oil drive performance and observed that they reduced the contact angle to zero and changed the core surface wettability from strongly oil-wet to strongly water-wet. Li et al. (2022) formulated a GO-enhanced polymer water injection system. Compared with traditional polymer systems, adding 0.15 wt% of GO resulted in satisfactory viscosity enhancement, shear resistance and age stability, and it also increased flooding efficiency up to 72.87%. Pandey et al. (2024) explored the potential of MWCNTs in enhancing the flooding performance of surfactants, and they observed that the addition of this material decreased the IFT of the original system by up to 56%. Besides, it also decreased the surfactant loss and changed the rock surface wettability from oil-wet to water-wet, yielding an EOR of up to 70%. Haruna et al. (2024) observed that the addition of GO notably increased the viscosity and thermal stability of HPAM. After aging at 80 °C for 30 days, the viscosity of HPAM decreased by only 6%, which is beneficial for high-temperature oil recovery.

Imbibition is another important flooding strategy for EOR in oilfield development. In this strategy, the wetting phase replaces the nonwetting one because of the capillary forces in low-permeability tight reservoirs. Imbibition determines the yield and recovery of crude oil. To this end, surfactants and silica nanoparticles have proved to be ideal additions for improved reservoir wettability (Meng et al., 2017). Mandal et al. (2016) investigated how a composite of the anionic surfactant SDBS and the nonionic surfactant Tween-80 influences rock wettability, and they observed that composite surfactants were considerably more effective than surfactant-only solutions. Zhao et al. (2018) prepared stable silica nanoparticle solutions with nonionic surfactants as a dispersant and synergists and used them in imbibition experiments. These nanoparticles could alter wettability from lipophilic to hydrophilic. The addition of SiO_2 increased the recovery by 16% compared to the surfactant-only system. Considering that silica nanoparticles are not widely used in oilfields, as they cannot be exposed to high temperatures and high salinity for extended periods, the authors switched their attention to carbon-based nanomaterials. They prepared hydrophilic carbon nanoparticles and added Tween-80 to uniformly disperse the nanoparticle fluid in the aqueous phase. The small particle size of the nanoparticle fluid enabled it to remain stable at high salinity and high temperature and achieve a spontaneous imbibition recovery of up to 24%; imbibition mainly occurred because of a decrease in capillary forces (Zhao et al., 2020). For low-permeability reservoirs, the authors prepared activated sulfonated silicon quantum dots, which remained stable even after exposure to 5 wt% NaCl at 120 °C for seven days. This notably increased the temperature and salinity resistance and resulted in an imbibition recovery enhancement of up to 29.9% (Zhao et al., 2023b). Sakthivel and Kanj (2021) investigated the efficiency of CDs and the Gemini surfactant GS8 on the imbibition recovery from carbonate rock samples via a series of spontaneous imbibition tests, and showed that the CDs performed considerably better, mainly because of increased capillary forces and wettability alterations.

3.2 Profile control and water shutoff

Profile control and water shutoff are effective means of enhancing water injection performance and stabilizing reservoir yield in oilfields (Fig. 6). The existing materials in profile control and water shutoff, such as gels and polymer microspheres, tend to be insensitive to external conditions.

However, nanomaterials offer a promising solution by improving the performance of polymer-based materials. Son et al. (2015) noted that emulsions stabilized using silica nanoparticles and polyvinyl alcohol (PVA) tended to have high stability. The addition of 0.05% PVA and 3% nanoparticles yielded the best emulsion stability and highest recovery, and the emulsions could serve as a sealant to seal 22.15-24.64 μm^2 of high-permeability pore channels. Tang et al. (2020) modified silica nanoparticles using 3-methacryloyloxypropyltrimethoxysilane and selectively yielded swellable polymer/nanosilica composite microspheres (PNSCMs). The incorporation of modified nanosilica greatly increased the thermal stability and viscoelasticity of the PNSCMs, affording them higher dispersion stability and sealing performance, with a maximum sealing rate of 93.64%. These PNSCMs are suitable for the deep profile control of reservoirs and thus possess vast application



(a) (b)

Fig. 6. Action mechanism of the plugging agent.

potential in oilfield development. CNTs feature low density, high mechanical strength and strong adsorption, and they are remarkable additives for increasing the strength and stability of host materials. Ito et al. (2012) fabricated a novel sealing material based on MWCNTs and a rubber nanocomposite for use in high-temperature, high-pressure reservoirs. This fabrication was achieved via surface treatment of MWCNTs to ensure that they were uniformly dispersed and stably bonded with the rubber matrix. Field test results demonstrated that the composite had high chemical stability and could withstand temperatures from -10 to 260 °C and pressures up to 310.26 MPa. Therefore, these can be employed for deep-profile control of high-temperature, high-pressure reservoirs. Lu et al. (2024) synthesized a modified nanographite (MG) with chemical cross-linking ability and prepared a hybrid cross-linked gel using PAM as polymer matrix and hexamethylenetetetramine, hydroquinone, and MG as cross-linking agents. The effects of MG on the gel formation time, gel strength and thermal stability were investigated and the blocking ability of MG hybrid cross-linked gels was evaluated. The results showed that addition of 0.2 wt% MG resulted in a gelation time of 4 h for the hybrid gel system, a maximum tolerable temperature of 154.9 °C, and enhanced thermal stability and water locking ability with a plugging rate of 90%, effectively plugging cores and decreasing permeability. Wu et al. (2024) constructed a surfactant-assisted Janus nanofluid *in-situ* emulsification and thickening system with IO and Tween 60 to effectively plug high-permeability layers and promote fluid flow. The high-permeability layer experienced a notable increase of 12.98%, while the oil recovery efficiency of the low-permeability layer also exhibited a significant improvement of 12.86% following the regulation of *in-situ* emulsion and viscosification system.

3.3 The fracturing process

As the global demand for oil and gas resources increases, unconventional resources are becoming a focus of petroleum research. These reservoirs have complex conditions, such as low permeability and low porosity, because of which hydraulic fracturing is usually employed to achieve EOR. Given their readiness for modification, nanomaterials can enhance the properties of fracturing fluids and are well applicable for high-temperature, high-pressure formation conditions (Wang et al., 2024).

The addition of nano-crosslinkers into fracturing fluids can enhance their fracture-forming and sand-carrying capacity. Nano-crosslinkers reported so far mainly include nano-boron crosslinkers, nano-zirconium crosslinkers, nano-titanium crosslinkers, and multisite crosslinkers loaded on nanosilica carbon materials. Jia et al. (2015) modified silica nanoparticles via surface amination and exposed them to borate ester to yield a nanoscale organic boron crosslinker, which could be added to fracturing fluids to form a gel. This new crosslinker effectively cross-linked hydroxypropyl guar gum, and the resultant fracturing fluid system exhibited good resistance to temperature and salt. Bello et al. (2022) presented a rheological study of GO-based cationic surfactant solutions as fracturing fluids. A content of 1-3 wt% surfactant in the fracturing fluid system generated a network of cylindrical micelles, and the addition of GO could increase the viscoelasticity of the system. Minakov et al. (2024) observed that SWCNTs as a nanoadditive considerably influenced the wettability of cross-linked gels for hydraulic fracturing and result in a threefold decrease in capillary absorption. The hydraulic fracturing process can be more flexibly controlled via adjusting the concentration, size, material, and morphology of these SWCNTs. Fracturing results in a complex network of fractures and microfractures in reservoirs. Since the particle size of the currently used conventional fracturing proppants is not large enough for them to be carried through the fracturing fluid into the microfracture, they often block microfractures, which impairs the flow conductivity of the fracture network of the reservoir. Bose et al. (2015) first introduced the idea of nanoproppants, which are injected into the formation prior to the use of conventional fracturing proppants so that they fill up the natural microfractures along the main fractures (Fig. 7). This not only props up microfractures but also contributes to the conductivity of the crack network. Haque et al. (2019) combined MWCNTs and phenolic resin into a nanocomposite resin-coated proppant. The results of laboratory tests indicated that this coating system greatly increased the compressive strength and conductivity of the proppant. The performance of the coated sand remained undeteriorated upon exposure to high temperatures, making it a suitable candidate for field app-

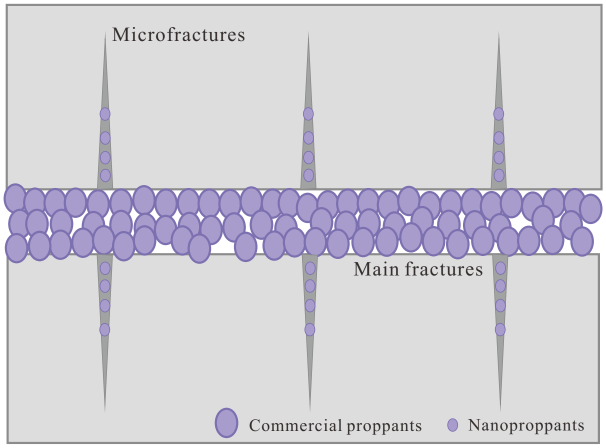


Fig. 7. Schematic of proppants and nanoproppants distributed in fractures and microfractures (modified from Bose et al. (2015)).

lications under higher stress conditions. Tabatabaei et al. (2019) modified the surface of a proppant matrix using graphite nanoplatelets (GNPs). The addition of GNPs greatly increased the conduction capacity and compressive strength of the proppant, altered the surface wettability, and made the surface highly hydrophobic. Using this proppant in the hydraulic fracturing of oilfields not only expedited the flowback of fracturing fluids but also resulted in a remarkable level of EOR.

Injection pressure reduction and injection enhancement are important means of EOR improvement. In this regard, nanomaterials have immense potential for decreasing injection pressure and EOR for the development of unconventional petroleum resources. They are an ideal solution for water injection operations facing challenges such as high pressure, low oil displacement speed, and low final recovery. This is because the extremely high hydrophobicity and high surface energy of nanomaterials enable them to be easily adsorbed onto the surface of rock pores and remove the surface water film upon entry into the formation, remarkably enlarging the flow pore diameter. Nanomaterials adsorbed onto a rock surface form a highly hydrophobic layer, which can decrease the injection resistance, increase the injection volume, and effectively prevent the clay from hydration swelling (Yang and Liu, 2021).

In oilfields, nano-polysilicon materials are commonly used as a pressure reduction injection enhancement agent. These are SiO_2-based, 10-20 nm spheroid nanoparticles that can be highly hydrophobic after chemical modification. Xiong et al. (2010) grafted a large amount of methyl on the surface of a nano-polysilicon injection enhancer, which exhibited high hydrophobicity. The addition of 0.2-0.25 wt% nanoparticles resulted in a tight hydrophobic film over the rock pore surface of the formation, greatly decreasing the flow resistance and increasing the aqueous permeability. Results of field tests indicated that this pressure reduction injection enhancement nanomaterial system had an effective period of 194 days, achieving an average pressure reduction of 12.75 MPa and injection enhancement of 2,359.3 m^3 per well. Because traditional nanomaterials have moderately large particle size, they tend to block formation pores and exhibit poor temperature and salinity resistance. In contrast, carbon-based nanomaterials are characterized by ultra-small particle size (< 10 nm) and readiness for modification, hence they have triggered wide interest. Wu et al. (2021) demonstrated that without adding any surfactant, a 0.2 wt% electrochemically synthesized hh-CDs nanofluid resulted in a pressure reduction of 23.81%. Wang et al. (2023) investigated the performance of the amphiphilic CDs C12-SCDs with a cationic surfactant (dodecyl trimethyl ammonium bromide, DTAB) and an anionic surfactant (sodium dodecyl sulfate, SDS). They also reported that the C12-SCDs could combine with the surfactants to form a hybrid adsorption layer and enhance wettability alterations, and that DTAB, SDS, C12-SCDs could collaborate for a decrease in surface tension. The pressure reduction rates for DTAB, SDS, C12-SCDs, DTAB/C12-SCD mixture and SDS/C12-SCD mixture were 10.42%, 11.54%, 22.91%, 26.32%, and 24.75%, respectively. DTAB/C12-CD and SDS/C12-CD mixtures could effectively remove oil films, refining the channel of injected water. These mixtures could also adsorb onto the surface of hydrophilic nuclei to form a hydrophobic surface and induce the hydrophobic slip of injected water, decreasing both surface tension and injection pressure. Li et al. (2023) synthesized active nanoparticles (sm-CDs) via a hydrothermal reaction, which resulted in improved surface activity at a reaction temperature of 90 °C and a salinity of 16×10^4 mg/L, decreasing IFT from 17.02 to 0.06 mN/m and lowering alkane-rock viscosity to 19.4 pN. The results of core flooding tests indicated that the addition of 0.03 wt% sm-CDs resulted in 63.5% pressure reduction and 23% recovery enhancement. All the above studies revealed novel flooding candidates for harsh reservoirs in unconventional oilfields.

4. Conclusions and prospects

The focus of future petroleum development is expected to gradually transition from conventional to unconventional oil resources, among which low-permeability oil reservoirs have become an important choice for China. During oil displacement, a significant portion of crude oil remains trapped in the throat structure of nanoscale pores underground, which conventional nanoparticles not only fail to penetrate but also they have poor temperature and salinity resistance, preventing them from being effective in formations under harsh underground conditions. Carbon nanomaterials provide a satisfactory solution to these problems, presenting a decent alternative for the high-quality exploitation of reservoirs. Moreover, as oilfields evolve towards intelligent operation and the integration of new energy sources, nanomaterials and nanotechnologies are expected to open up new avenues for upgrading to quantum technology and artificial intelligence for optimized oil displacement strategies. Accordingly, nanotechnologies possess vast application potential for the future petroleum engineering industry.

Petroleum production byproducts such as asphalt and petroleum coke can be used as a source of nanomaterials to minimize production costs, reflecting the development trend of nanotechnology towards scaling up and cost effectiveness. Currently, nanotechnologies are already widely applied in various areas of EOR, such as high-efficiency oil displacement, profile control and water shutoff, as well as the fracturing process. For example, materials such as CDs, CNTs, and graphene are being synthesized via electrochemical reaction, CVD, and laser etching. Their small size and high stability enable the oil displacement of conventional and unconventional petroleum resources at low cost and high efficiency, providing a direction for high-quality oilfield development in the future. However, some problems with nanomaterials still persist:

1) They are limited by large-scale development costs and preparation techniques, facing the complex geological environment of the reservoir. Practical applications are influenced by a variety of factors such as rock pore structure, reservoir type and fluid characteristics. Besides, field applications necessitate a lot of experiments and adjustments, and large-scale application has not yet been achieved.
2) The aggregation of carbon-based nanomaterials in the formation will affect the performance of EOR. The key to solving aggregation is the further development of long-term stable carbon nanofluids, especially in harsh environments with high temperature and salinity.
3) The behavior of carbon nanofluids downhole and their compatibility with the formation environment are still unclear and need further in-depth research.
4) The effects of the highly active carbon-based nanomaterials on aquatic organisms or microbial communities and their degradability in the environment have not been clarified, nor have studies targeted their ability to be recovered and recycled.

Future research should include the following aspects:

1) Promote the preparation of low-cost and environmentally friendly carbon nanofluids by using cheap and readily available organic solid waste as carbon sources, such as petroleum industry by-products, biomass, etc., and facilitate the industrial application of carbon nanomaterials in EOR.
2) Develop multipurpose composite nano-flooding systems. Carbon-based nanomaterials have a multitude of modifiable active sites on their surfaces. Functional design and modification of the properties of the materials can be carried out in combination with the actual needs of the field, so that the carbon nanofluids can maintain good dispersion and avoid particle agglomeration, enabling their efficient application to oilfield development.
3) Investigate the flow pattern and dynamic imbibition of carbon-based nanomaterials by nuclear magnetic resonance. Intuitively study the microscopic seepage of fluids, explore the interaction of carbon-based nanomaterials in reservoirs and the dynamic evolution mechanism focusing on assessing the depth of use of these materials.
4) Explore the interactions and potential biological impacts that exist between nanomaterials and subsurface microorganisms and flora through the close integration of environmental science and biology. Develop efficient recycling methods of materials.
5) Advance oilfield development towards intelligent technology. Nanorobots and reservoir nanosensors are expected to be able to collect and analyze the formation parameters, which might break the barriers of unconventional energy extraction and is of great significance for the effective exploitation of oil resources.

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Conflict of interest

The authors declare no competing interest.

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