# Surface modification of nanoparticles to improve oil recovery Mechanisms: A critical review of the methods, influencing Parameters, advances and prospects

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## ARTICLE INFO

## ABSTRACT

The utilization of nanoparticles (NPs) in enhanced oil recovery (EOR) has a lot of benefits however, the usage of bare NPs still has a few drawbacks, including instability, agglomeration and aggregation, which can cause pore channel obstruction and quick sedimentation resulting in low oil recovery. Nonetheless, surface modification of NPs can circumvent these problems however, an account of leading approaches for surface modification and their effect on improving EOR effectiveness interconnected with NPs microscopic features, with the aim of providing a guide for future efforts in this area is essential. Here, a critical review on surface modification of NPs to improve oil recovery mechanisms is presented. Surface modification of NPs can be classified into two categories: in-situ surface modification and post-synthesis surface modification, both of which involve grafting, coupling, surfactant usage, and esterification to achieve the same results. Surface modifications can reduce particle hydrophilicity, reducing particle retention on rock surfaces. Depending on the NPs' surface nature, many techniques based on surface affinity for different chemical groups have been created. The study equally revealed that functionalized NPs have excellent mobility regulation, thermal stability and rheological properties, and they make oil droplets stable against coalescence. Moreover, the application of different surfaced modified NPs in EOR were reviewed. Finally, the challenges encountered were identified with proffered solutions, future trend and research opportunities were outlined. Since each modification type is tailored to the final application, there is no single best NPs surface modification technique. As a result, when it comes to specific goals, all techniques are equally weighted.

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## Contents

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**Nomenclature**

*List of Acronyms*

| | |
|---|---|
| Al2O3 | Aluminum oxide |
| BT | Breakthrough |
| CA | Contact Angle |
| CaCO3 | Calcium Carbonate |
| CEOR | Chemical Enhanced Oil Recovery |
| CTAB | Cetyl Triamonium Bromide |
| DBSA | Dodecyl benzene sulfonic acid |
| EOR | Enhanced Oil Recovery |
| Fe2O3 | Ferrous Oxide (Iron Oxide) |
| HPAM | Hydrolyzed Polyacrylamide |
| HPHT | High pressure and high temperatute |
| KH540 | 3-aminopropyltrimethoxysilane |
| IFT | Interfacial Tension |
| IOS | Internal Olefin Sulphonate |
| LHP | Lipophobic and Hydrophobic Polysilicon |
| MMTS | Methyl trimethoxy silane |

| | |
|---|---|
| Na-Mt | Sodium Montmorillonite |
| NFs | Nanofluids |
| NPs | Nano Particles |
| O/W | Oil water contact |
| °C | Degree Celsius |
| ° | Degrees |
| PAM | Polyacrylamide |
| PEG | Polyethylene Glycol |
| PH | Hydrogen Potential |
| PTMS | Trimethoxypropylsilane |
| PVP | Polyvinylpyrrilidone |
| SDBS | Sodium Dodecyl benzene sulphonate |
| SiO2 | Silicon Dioxide |
| SPN | Super permanganate |
| TiO2 | Titanium dioxide |
| ZnO | Zinc Oxide |
| ZrO2 | Zirconium Dioxide |

## 1. Introduction

Crude oil and natural gas, remain the world's key energy sources despite the quest for renewable energy [1]. Nevertheless, only about two-third of the original oil in place (OOIP) can be recovered during the primary and secondary stages of oil extraction, while significant quantities of oil remain in reservoirs [2]. Enhanced oil recovery through chemical means (CEOR) has proven to be an efficient tool in recovering bypassed oil in reservoirs. The bypassed oil is caused by reservoir heterogeneity or an unfavorable mobility ratio between the injected fluid and displaced fluid. Residual oil, on the other hand, is made up of discrete ganglia that develop as an oleic mass protrusion produces a narrow neck because of the combined effects of local pressure gradient and interfacial tension (IFT) [3]. To recover the bypassed oil, surfactants are used to reduce IFT and alter the wettability between the rock and fluid. Whereas polymers are used to increase the viscosity of the injected fluid, to decrease the mobility ratio between the injected fluid and the displaced fluid. Alkali–surfactant (AS), surfactant/polymer (SP), alkaline/polymer (AP), and alkaline/surfactant/polymer (ASP) are chemical EOR (CEOR) slugs. In oil wells, the synergy of the combined conventional chemicals boosted efficiency. Recent studies have demonstrated that foam enhanced with surfactants and polymers for greater stability and mobility control can improve oil recovery [4]. However, surfactants have the disadvantages of adsorption on the reservoir rock surface, whereas the degradation of polymers at high salinity and high temperature condition has hindered their performance in recovery bypassed and residual oil [1,4,5]. The advent of nanotechnology, on the other hand, presents a once-in-a-lifetime potential to transform the oil and gas industry in the upstream, downstream, and midstream sectors. The Nano-solution acts as a property modifier, lowering the IFT and easing the transition from oily to watery wettability, as well as modifying the rheology of formation fluid in situ [6]. The usage of NPs in the petroleum industry is mostly due to their nanoscale dimensions, which reveal intriguing properties and enable the modification and control of several elements in comparison to their large-scale equivalents [7]. Despite the fact that NPs can improve all of the aforementioned features, they nevertheless face a number of difficulties when used in EOR operations without surface adjustments. Some of the difficulties encountered include rapid agglomeration and aggregation, low dispersibility, and pore channel obstruction. Nonetheless, the surface modification of NP can enhance oil recovery mechanisms compared to the unmodified [1]. This is because surface modification of NPs can prevent nonspecific binding, aggregation and sedimentation, mak-

ing the NP more stable when dispersed in base fluids [8], and as a result, can filter through pore channels with little retention. Furthermore, surface modification can introduce other functional groups which can prevent oxidation and act as a perfect protection for the NP. These functional groups can act as a connecting unit to attach other functional polymers or surfactants. For example, Lui et al. [9] used surface modification and chemical etching to establish a novel functional Janus-SiO$_2$ NP with size 4–9 nm and specific surface area of 612.9 m$^2$/g. Consequently, a significant increase in viscosity of hydrolysed polyacrylamide (HPAM) by 282.9% resulting in about 36.6% oil recovery. Li et al. [10] studied the effect of several NP surface treatment methods on the stability of SiO$_2$ NP at reservoir condition. Their results indicate that hydrochloric (HCl) acid and polymer surface modification were stable for months and can improve NP stability at reservoir condition.

Although a lot of original research on NP surface modification has been published in recent years, and it has provided insight into some novel methods that can be applied in technology, a full assessment of leading methodologies for surface modification and their effect on boosting EOR effectiveness interconnected with NPs microscopic aspects is elusive in order to give a direction for future efforts in this field. Therefore, this paper presents a critical review on surface modification of NP to improve oil recovery mechanisms. The majority of surface modifications of NPs in the literature have occurred at low temperatures. Temperature, on the other hand, is critical in the process. Bonds are broken and reformed at desired temperatures, which is an important factor in governing NP surface modification. More research on the surface modifications of NPs at different temperatures is thus required. The concepts discussed in this paper can benefit pharmacist, chemist, material and chemical engineers. Hence, NP surface modification methods were discussed. Subsequently, the factors influencing NPs surface modification were elucidated. Likewise, the effect of NPs surface modification on EOR mechanisms were presented. Moreover, application of surface modified NPs in EOR were reviewed. Finally, the challenges encountered were identified with proffered solutions, future trend and research opportunities were outlined.

In the first part, NPs surface modification methods such as coupling, grafting, esterification and the use of surfactants were discussed in detail. Factors influencing surface modification which include surface charge, pH, zeta potential (ZP), ionic strength, temperature and surface chemistry were presented in the second part. The third part focused on the effect of NPs surface modification on EOR mechanisms like IFT, wettability, fluid viscosity, asphaltene precipitation and emulsion. The fourth part was dedicated to the application of surface modified NP in EOR, a summary of the important results and outcomes from recent studies were reviewed. The last part outlined the challenges, opportunities and future trend for surface modified NPs.
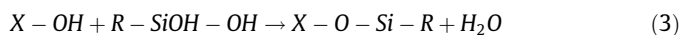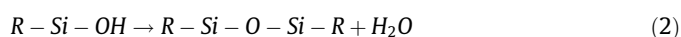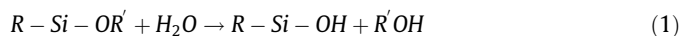
## 2. Nps surface modification methods

NPs surface functionalization is a method that attempts to develop and/or apply properties that can be used in a variety of research and engineering applications. It refers to the nanoscale assembly of various organic and inorganic materials unto the surface of NPs using covalent or noncovalent bonds such as hydrogen bonds, electrostatic force, or van der Waals force. There are two types of surface functionalization of NPs: in-situ surface functionalization, which occurs during synthesis, and post-synthesis surface functionalization, which occurs after the particle has been completely synthesised. Both approaches work on the same principle. In situ surface functionalization, as opposed to post-synthesis surface functionalization, can give particles with substantially

smaller diameters [11]. This is achievable since they are functionalized immediately after synthesis with less agglomeration. In porous media, the filtration, adsorption, and rheological behaviour of nanomaterials are determined by its surface chemistry. Consequently, appropriate surface adjustment controls particle characteristics which in turn improve emulsification, improve foam stability, decrease particle retention and wettability [12]. In most cases, the first step of surface modification involves using homo- or hetero-bifunctional cross linkers to incorporate an organic functional group (R-NH2, R-COOH) that can be used to bind to the particle and enhance its properties. For instance, the surfaces of NPs can be adjusted with organic functionalities to prevent agglomeration and inadequate dispersion in base fluids [13]. Thus, improving the displacement efficiency of oil compared to bare NPs. The common surface modifications techniques in the literature are coupling, esterification, surface graft polymerisation and the use of surfactants [244]. Generally, NPs surface modification methods are heavily reliant on the materials. Coordination interactions are frequently engaged in bonding connections with functional ligands for NPs with metal sites. A schematic of the main surface modification methods of NPs is illustrated in Fig. 1.

### 2.1. Coupling

Coupling agents are a diverse group of chemical substances that include fatty acids and their salts, such as calcium stearate, as well as organofunctional silanes, which are commonly employed to modify the surface of NPs. A portion of the group in the molecule can form a close chemical bond with different functional groups on the NPs surface, while another portion may undergo a chemical reaction or physical entanglement with an organic polymer. As a result, the binding agent is referred to as a "molecular bridge" because it improves the interfacial contact between inorganic and organic substances, thus significantly enhancing the composite material's performance. Silane coupling agents are mostly used in coupling due to their unusual bifunctional configuration with one end capable of reacting with the silanol groups on metal oxides surface and the other end compliant with polymers. This technique has drawn a lot of interest for treating oxides filler [15]. Fig. 2 illustrates the schematics of NPs silane coupling agent. The hydrolysis and condensation processes of silane coupling agents make them adhere to the metal oxide surface [16]. The coupling agent is dissolved in water (Equation 1), ethoxy groups are hydrolysed and Si–O–Si bonds are generated (Equation 2). The alkyl groups of the coupling agent are then deposited on the surface of the NPs by reacting with the hydroxyl groups of metal oxide NPs through condensation (Equation 3).

$$R - Si - OR' + H_2O \rightarrow R - Si - OH + R'OH \qquad (1)$$

$$R - Si - OH \rightarrow R - Si - O - Si - R + H_2O \qquad (2)$$

$$X - OH + R - SiOH - OH \rightarrow X - O - Si - R + H_2O \qquad (3)$$

whereas R and R' are functional groups (ethyl or methyl) and X is metal oxide, respectively. Nguyen et al. [17] performed a laboratory test on the coupling of titanium oxide (TiO$_2$) with silane and discovered that particle agglomeration was minimised after the modification procedure, and excellent stability was achieved. Mallakpour et al. [18] used various dicarboxylic acids to modify different metal oxide NPs. According to their results, the surface of zirconium oxide (ZrO$_2$) NPs, was updated with bioactive diacid N-trimellitylimido-l-leucine. Diacid was grafted on the surface of ZrO$_2$ to increase dispersion, and the resulting NPs were used as filler in a poly(amide–imide) (PAI) matrix [18]. Likewise, to improve the dispersion potential of NPs in polymeric matrix, copper oxide (CuO) and TiO$_2$ were
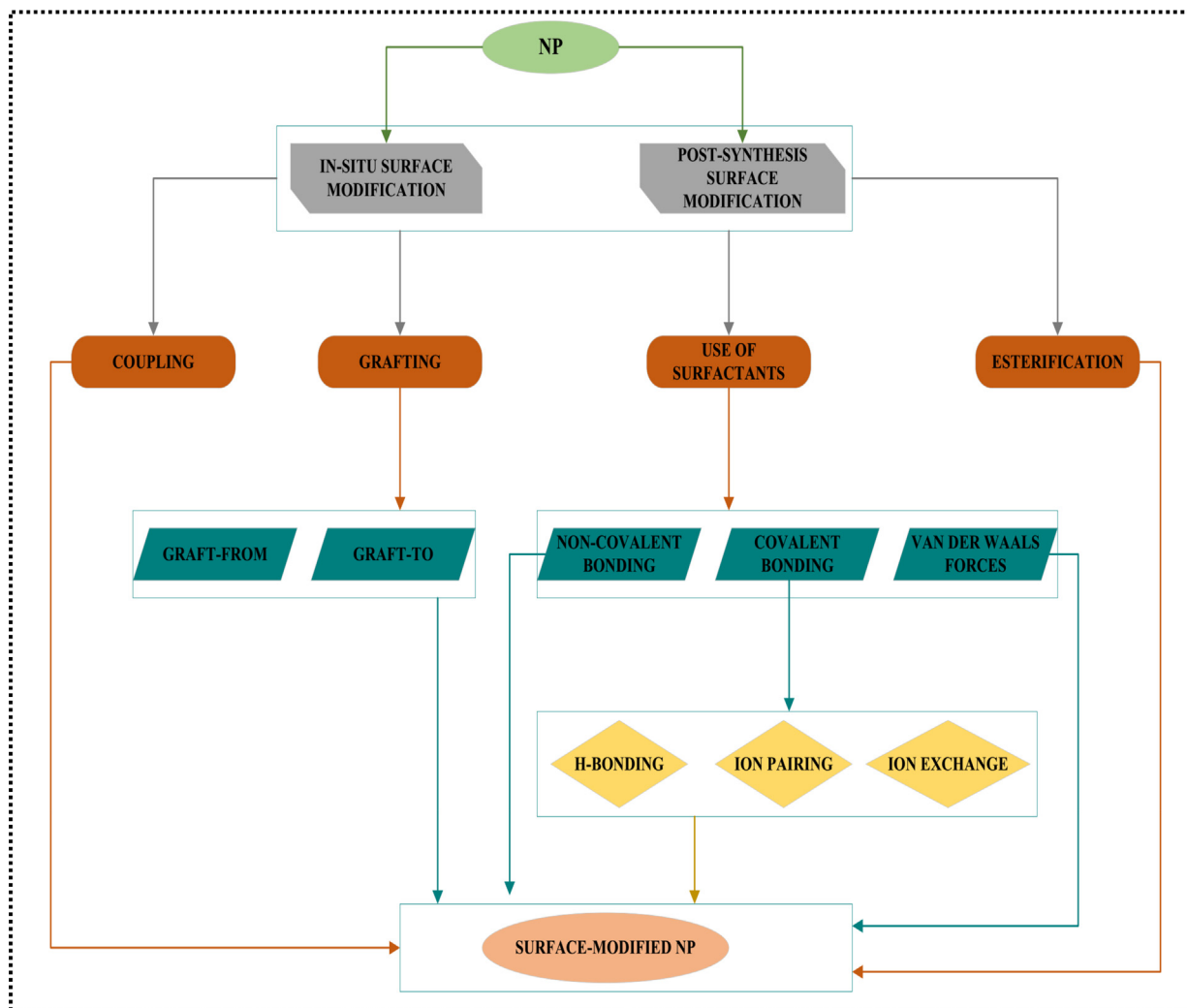
**Fig. 1.** A Flowchart Illustrating the Main Methods for NP surface Modifications.
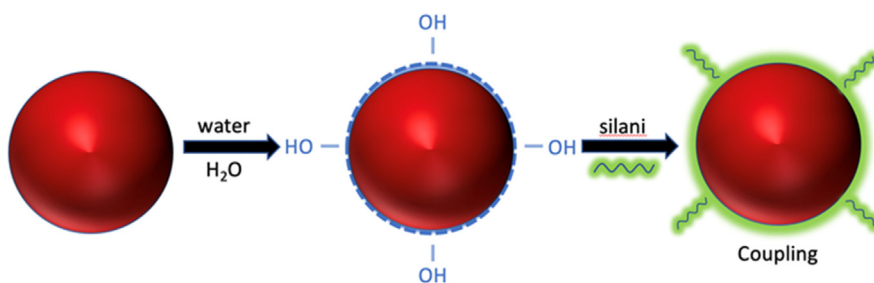


**Fig. 2.** Schematic Illustration of Silane Coupling of NPs.

updated with a bioactive diacid N-trimellitylimido-l-valine as a coupling agent [19,20]. In another study, bioactive dicarboxylic acids containing various natural amino acids such as l-valine, l-methionine, l-leucine, and l-isoleucine were used to modify the surface of TiO₂ NPs with an average diameter of 30 nm. Bioactive DAs were effectively coated on the surface of TiO₂ as coupling agents. The attachment of the modifier molecules on the surface of TiO₂ NPs were found to be in a bidentate chelating mode with ester linkage, according to Fourier transform infrared spectroscopy (FT-IR) studies. Each coupling agent's OH group reacted with OH groups on the surface of TiO₂ NPs [19]. Surface modification of NPs by cou-

pling causes the NP's dynamic size to rise. Unmodified NPs, on the other hand, tend to clump together and create larger clusters. As a result, coupling minimises agglomeration and hence restricts the creation of such clusters, resulting in NPs with improved characteristics.

*2.1.1. Esterification*
Esterification is a chemical reaction in which two reactants such as alcohol and acid combine to create an ester as the reaction product. The formation of esters from carboxylic acids is called esterification. Specifically, when a carbon is linked to two oxygens, one of

the oxygens is double bonded to the carbon while the other oxygen is attached to another carbon. When a carboxylic acid interacts with an alcohol, esterification occurs. Only an acid catalyst and heat are required for this reaction to take place. The removal of the –OH from the carboxylic acid requires a lot of energy, thus a catalyst and heat are required to provide the required energy. The most important feature of esterification surface alteration of NPs is the transformation of the initial hydrophilic and oleophobic surface to a lipophilic and hydrophobic surface and it's most common with nanocellulose. The functionalization of NP (Fig. 3) occurs in six steps during esterification with the help of a carboxylic acid in the presence of an alcohol and an acid: Formation of cations, Transfer of proton, where a proton is transferred to one of the hydroxyl groups to make a good leaving group., delocalized carbocation, where the carboxyl oxygen is protonated to give a delocalized carbocation, making the carbocation a better electrophile. The pi($\pi$) bond is formed when the alcohol oxygen atom of the hydroxy group gives a pair of electrons to a carbon atom, forming a bond by removing water. Because water has a lower concentration than methanol, it is not a viable nucleophile for reversing the process. The ester group then replaces the OH group on the NP. During the esterification process, the reaction happens either on the cellulose polymer chains, forming typical cellulose esters, or on the outer surface of the cellulose fibres, leaving the cellulose crystalline structure intact. To produce a large number of cellulose esters, both homogeneous and heterogeneous esterification can be used [21]. Furthermore, reactions under heterogeneous circumstances may be used almost entirely for surface modification of native cellulose, which is also one of the major techniques for nanocellulose separation and chemical modification [14]. Leszczynska et al. [22] investigated the surface modification of cellulose nanocrystals (CNC) with sodium hydroxide (NaOH) and discovered that the degree of surface substitution of CNC increased with the molar ratio of succinic anhydride to cellulose hydroxyl groups (SA: OH), as well as reaction time, while the reaction temperature had a moderate effect on the degree of esterification. In pyrolytic and oxidative atmospheres, research on the thermal durability of modified NPs revealed that there is a threshold degree of surface esterification below which only a small drop in the initial temperature of degradation was found.

Where O stands for oxygen, H for hydrogen and R, R' and R" are functional groups, respectively.

### 2.1.2. Use of surfactants

Surfactant molecules are made up of two distinct components: an oleophilic group that has an affinity for oil or organic matter, and a hydrophilic group that has an affinity for water or an inorganic material. Surface Modification of NPs with the use of surfactants can be achieved either using chemical or physical adsorption. Physical adsorption is typically accomplished via the adsorption of surfactants or macromolecules onto the NPs' surface. The polar group of a surfactant is preferentially adsorbed to the surface of the NPs by electrostatic contact in this type of surfactant treatment [23]. Chemical modification, on the other hand, usually involves the formation of a covalent bond with the reactive NP, which results in the release of a hydrogen molecule as a biproduct. This type of surface modification is common with molecules with a thiol group [24]. Surfactant's structural properties enable it to be used in surface modification of NP, converting the hydrophilic groups on their surfaces to oleophilic groups, increasing the NPs' affinity for organic compounds, as well as their compatibility and dispersibility [25]. Surfactants have been used to enhance the stability of NPs in several reports [26]. Roy et al. [27] used cationic surfactant cetyltrimethylammonium bromide (CTAB) to modify the surface of $TiO_2$ NPs and discovered that when CTAB was added to the $TiO_2$ surface, ionic interaction between positive and negative charges occurred on the surface of $TiO_2$ NPs. As a result, the $TiO_2$ NPs were surrounded by a lengthy organic chain of CTAB. Finally, CTAB interacted with the surface hydroxyl groups of $TiO_2$ NPs, grafting CTAB onto their surface.

The existence of electric double layers of varying strength and charge density influences the surface modification of NPs with surfactants, along with nanocrystal development and assembly. To preserve charge neutrality, $SiO_2$ surfaces with a negatively charged oxide ($SiO^-$) surface at pH 7 form a double layer of negative ZP with connected and fragmented cations or positively charged surfactant head groups. To complete the electric double layer of titania with low pH values of 3, the surface layer includes of positively charged $TiOH^{2+}$ groups and adjacent compensatory anions such as $Cl^-$ or alkaline surfactants. The chemistry and reactivity of the surface then dictate the conditions where covalent-cross bonds can form and remain stable [28,29]. Surfactants have a critical role in colloidal stability and NP dispersion in particular solvents [30,31]. When no surfactants are present, metal NPs produce amorphous reaction products like palladium black, whereas oxide nanostructures, mineral NPs, and due to polar and ionic surface interactions, quantum dots can clump together. [32]. [30]. Surfactants then give NPs unique surface hydrophobic or hydrophilic qualities, allowing them to disperse in a desired liquid like water, brine, alcohol, or octane.

Surfactant grafting processes may be classified into two categories: noncovalent adsorption and covalent assembly. Surfactant covalent grafting can be done in a few different ways. Thiol-end-group surfactants are frequently used to bind metals while hydrogen is eliminated, resulting in a 20–60 kcal/mol metal-sulfur bond energy. [31]. Ion exchange, ion pairing, and hydrogen bonding are
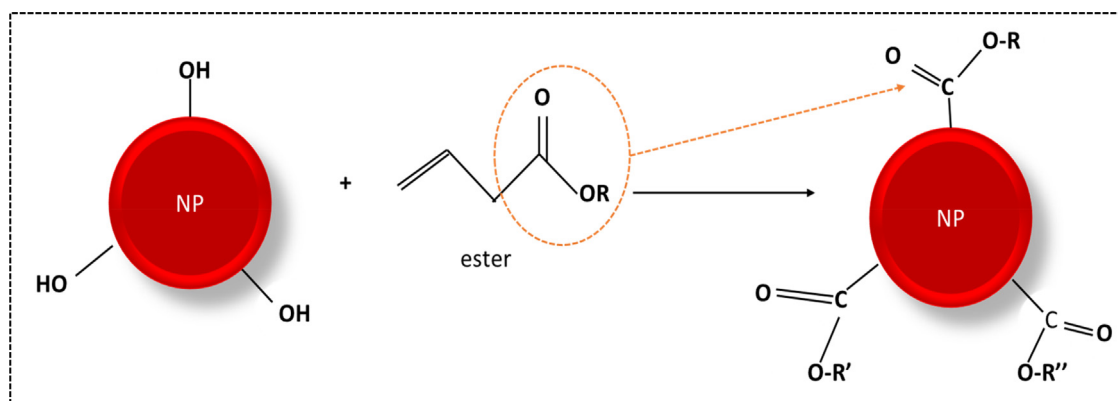


**Fig. 3.** Schematic Illustration of Esterification Modification of NPs.

all non-covalent adsorption methods [33,34]. Ion pairing differs from ion exchange in that it is a balance procedure that lowers the detected ZP by neutralising the surface charge, ion exchange, on the other hand, is a process that involves the substitution of a relatively continuous ZP that is frequently followed by flushing out the exchanged salts over the surface, eliminating them from the equilibrium, as shown in Fig. 4. [31]. When working with surfaces that contain acidic or basic groups, ion exchange is prevalent, however it is not necessarily accompanied by a change in ZP. Soft epitaxial contacts on metal surfaces, conformation effects, dispersion interactions, and depletion forces are all common interactions. [35-37]. Hydrogen bonding is another typical adsorption contributor; however, it is weaker than soft epitaxial, ion pairing and ion exchange, contacts [31].

Surfactants can equally be grafted onto NPs surfaces to give them new functions by interacting with the surrounding surfactant layer via van der Waals and electrostatic communications. This method can be used to create new compounds based on colloidal nanocrystals, which can then covalently link to produce new elements and features.

*2.2. Surface graft polymerisation*

Surface graft polymerization is a chemical reaction that bonds a polymer substance to the surface of an inorganic particle. Any of the hydroxyl or unsaturated bonds found on the surface of some inorganic particles (such as $SiO_2$, $TiO_2$, aluminium oxide ($Al_2O_3$) can be used directly to graft the polymer, or the hydroxyl group can be further reacted before grafting [38]. Grafting polymer molecules on the surface of NP has a stronger benefit than using surfactants or binding agents in that it not only increases NP dispersion stability but also improves NP interaction with resin matrix [39]. The presence of polymer chains on the surface of NPs can equally improve their surface properties, lowering IFT and altering the wettability of rock surfaces [40]. Grafting uses several different polymerization techniques, including radical, anionic, and cationic

polymerization. Several experimental factors, such as monomer content, NP dispersion, can be used to alter the thickness of the polymer capping layer. Because the NPs and polymer matrices are miscible, this technique is preferred for the production of NP–polymer nanocomposites [41]. Hydrophobic interactions, hydrogen bonding, and electrostatic interactions are examples of weak intermolecular interactions that can be utilised to alter the NP surface. This method allows ligand molecules to be conjugated quickly and easily without the use of any extra chemicals.

During the surface graft polymerisation process, there is physical adsorption onto the surface of NP as well as covalent grafting. Both polymer and NP are synthesized individually and connected in the reactor. In general, there are four methods for grafting polymeric chains to NPs: grafting to, grafting from, templated, and in situ polymerization or encapsulation [42]. All four methods produce polymer-grafted NPs with different shell architectures. The covalent bond formation compensates for the entropy loss caused by the polymer chains stretching away from the surface, resulting in the polymer graft conformation on the NPs. The harvested NPs are often blended with virgin polymer to generate polymer nanocomposite, if the polymer chains on the grafted NPs have a molecular weight lower than the entanglement molecular weight. If the molecular weight of the polymer chains on the polymer-grafted NPs is much higher than the entanglement molecular weight, a nanocomposite can be created without the use of an external polymer matrix [43-46].

- In the first method, the polymer chain grows in situ from an initiator that is previously anchored to the NP surface. The grafting then begins where the polymerizable groups (monomers) anchor themselves onto the initiator sites on the surface of the NP forming NP-Polymer nanocomposite [47].
- In the second method, hairy NPs are synthesised using a block copolymer-based micelle template. A precursor, usually a metal salt or an organometallic molecule, is loaded into the centre of polymer micelles made of either multimolecular block copoly-
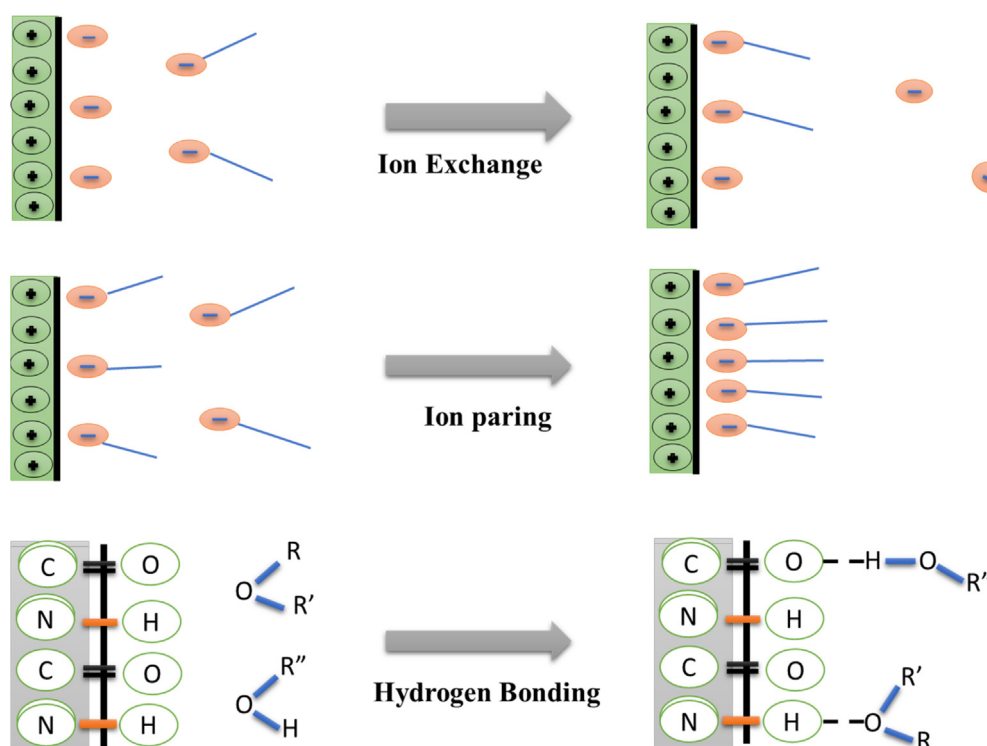


**Fig. 4.** Ion pairing, ion sharing, and hydrogen bonding as examples of Surfactant non-covalent adsorption processes on NPs in solution.

mer or unimolecular star block copolymer in this process. Core–shell NPs are generated by reducing (complex) metal ions in the micelle core [48,49].

- The third method is grafting from, which entails developing polymer chains straight from the surface of NPs that have been functionalized with appropriate initiator functions. The surface-initiated controlled radical polymerization approach for the synthesis of polymer-grafted NPs has shown significant advancements [50,51].
- The fourth method is grafting-to, which entails attaching end-functionalized polymer chains to the surface of NPs using appropriate chemical processes. Esterification, sialylation, click reactions such as thiol-ene, alkyne-azide cycloaddition, and other reactions have typically been used in this grafting to method [52,53]

Due to its capacity to produce well-defined polymer structures of desired composition and molecular weight, as well as a shell of regulated thickness on the NPs surface, grafting from method is frequently used in the polymer functionalization of NPs (Fig. 5). The "grafting from" method has equally been thought in numerous literatures to be preferable for sterically stabilising NPs in a polymer matrix because it allows for higher grafting densities and thus larger polymer coverages of the NP surface. When both types of polymers grafted NPs are deposited in a matrix with the same chemistry as the grafts, Zhao et al. [54] found that the physical adsorption technique (or essentially the "grafting to" process) results in improved miscibility when compared to "grafting from" NPs at comparable grafting densities. To explain these findings, Asai et al. [55] argued that, although (monomer-sized) grafting agents can be randomly placed on the NP surface in the "grafting from" approach, the "grafting to" protocol must consider the volume effect of the already adsorbed polymer chains. As a result, the "grafting to" method produces a broader and more uniform polymeric coverage of the NP surface than the "grafting from" method at a given grafting density. With all these controversies, the best method for surface graft polymerization of NPs is still debatable though in my opinion, I recommend the 'grafting from' approach because the grafting process takes place randomly in the reaction medium and controlling the volume effect of the already adsorbed polymer chains as reported by Asai et al. [55] might be difficult as in the case of 'grafting to'.

Tang et al. [56] proposed a mechanism for resolving the tendency of inorganic NPs to aggregate. In their article, high grafting efficiency zinc oxide (ZnO)/polystyrene composite NPs was made by anchoring 4,4 -azobis (4-cyanovaleric acid) (ACVA) onto the surface of ZnO NPs and then using its azo ($R - N = N - R'$) group to start polymerization of styrene monomer to make composite NPs. Zhang et al. [57] created grafted-silicon NPs made of poly (methyl methacrylate) and investigate the effect of reaction parameters on the grafting architecture. Penaloza and Seery [58] showed how to create polymer-tethered clay nanocomposites via a surface-initiated method. The authors demonstrated a robust approach for increasing dispersion in polymer nanocomposites by regulating and adjusting the design of the tethered polymer brushes on the clay surface. LaNasa et al. [59] provided a novel in situ strategy that balances enthalpic and entropic components in the search for well-dispersed polymer nanocomposites, extending grafting techniques to understudied immiscible systems. Table 1 summarizes the different surface modification methods of NPs with improved properties ranging from dispersion stability, particle retention through porous media and reduced aggregation.

## 3. Factors influencing NPs surface modification

Due to their large surface area, chemical reactivity, and high surface energy, NPs suffer from two significant issues: fast agglomeration and oxidation [76]. As a result, compatibility of NPs needs proper surface modification. To conjugate organic or inorganic compounds onto the surface of NPs, coating technique is the most popular surface modification strategy. This technique not only prevents NPs from oxidising and agglomerating, but also allows for further functionalization [77]. Surface modification of NPs has four primary goals: to increase or modify NPs' dispersion; to improve NPs' surface activity; to improve NPs' physicochemical and mechanical characteristics; and to improve NPs' biocompatibility [78]. A variety of variables impact the surface modification of NPs in various ways. In a dispersion fluid, NP surface modification may influence particle characteristics such as surface charge, size of particles, and ionic interactions whereas the dispersion fluid properties such as temperature, pH, and ionic strength may alter surface modification. Furthermore, surface modification is strongly influenced by the initial surface chemistry of the NP, which is determined by the kind of NP.

### 3.1. Surface Charge, pH and ZP

The surface charge of NPs is the net electrostatic charge of the particles [173]. It is characterized by ZP, which can be utilised as a qualitative indicator to adjourn dispersion stability. The pH of a sample in aqueous medium is one of the most critical variables affecting its ZP. Considering a particle suspended in a liquid with a negative ZP. When more alkali is added to the suspension, the particles become more negatively charged. If acid is introduced to this solution, the charge will be neutralised at a certain point. A build-up of positive charge will occur if more acid is added. The pH sensitive behaviour of the particles is derived from changes in electrostatic interactions between the particles, with attraction
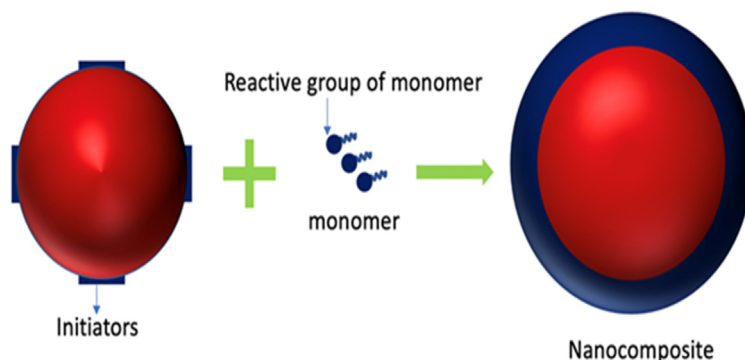
**Fig. 5.** Surface graft polymerisation process to yield polymer-nanocomposite.

**Table 1**
Summary of NPs Surface Modification Methods.

| NP | Modification Method | Finding | References |
|---|---|---|---|
| iron oxide ($Fe_2O_3$) | coupling using amino polysilanes | Improve dispersion stability | Jadhav et al. [60] |
| ZnO | $SiO_2$ Coupling | Reduces toxicity | Ramasamy et al. [61] |
| $ZrO_2$ | dicarboxylic acids esterification | Increase in dispersion and stability | Mallakpour et al. [18] |
| ZnO | Surfactant grafting with sodium dodecyl benzenesulfonate (convert hydrophilic groups on NPs surfaces to oleophilic groups) | Minimized the particle retention in porous media, reduced residual oil saturation and increased the oil recovery | Adil et al. [62] |
| ZnO | APTES coupling on the ZnO NPs | Improved Stability less prone to aggregation and sedimentation | Rabin et al. [63] |
| $SiO_2$ | sodium dodecyl sulphate (SDS) and CTAB (group altering) (surfactant grafting) | The adsorptive behaviour of a nanoparticle-surfactant composite material can be introduced at reservoir temperature without major changes in the adsorptive behaviour. | Betancur et al. [64] |
| $Fe_2O_3$ | Esterification with Citric acid, ascorbic acid and tetrahedral orthosilicate (TEOS) | Increase in gelling time of NPs NPs homogenously dispersed in gellant | Sabzi et al. [65] |
| $Al_2O_3$, CuO, $TiO_2$, ZnO, and $ZrO_2$ | SDS, CTAB and Triton X-100 (TX 100) group altering by grafting | Increased their dispersing ability Reduction in IFT | Yakeen et al. [66] |
| $Fe_2O_3$ | Grafting polymerisation of NPs with polymer ($C_6H_9NO_3$) | Change in surface morphology and enhancement in stability | Shalbafan et al. [67] |
| $SiO_2$ | Coupling with APTES | Reduced aggregation, improved oil recovery, increase in particle distribution and enhanced stability | Ngouangna et al. [1] |
| $TiO_2$ | Coupling with (3-aminopropyl) triethoxysilane (APTES) | Decrease in agglomeration. 97.7% grafting efficiency, excellent stability | Nguyen et al. [17] |
| $Fe_3O_4$ | Chitosan Coupling | High density immobilised molecules | Stolyar et al. [68] |
| $SiO_2$ | zwitterionic surfactant to alter the oleophilic group of NP (surfactant grafting) | Decrease surfactant adsorption | Zhong. [69] |
| $Fe_2O_3$ | Coupling with trimethoxysilane | Improved colloidal stability in hydrogen gels | Ahmadi et al. [70] |
| $SiO_2$ | Amine Coupling | Reduced severity of lung injury and neutrophilic filtration | Inoue et al. [71] |
| ZnO | Coupling with vinyl triethoxysilane | Super hydrophobic behavior and improved dispersibility | Nikhita et al. [72] |
| MgO | Silane coupling | Improved tensile strength | Akhtar et al. [73] |
| $Fe_3O_4$ | Coupling with triethylenetetramine | Increase specific absorption | Jiang et al. [74] |
| $Fe_3O_4$ & $SiO_2$ | Coupling with glycine and Malic Acid | Core – shell spherical shape NPs (change in morphology) | Alterrary et al. [75] |

and repulsion playing a key role in low and high pH environments, respectively [79]. This phenomenon is because different electrostatic interaction behaviour of particles in different pH is produced by simple protonation differences rather than irreversible chemical changes. The pH sensitive assembly and disassembly process is completely reversible [80]. In most reports, stability is one of the key factors that influences NPs surface modification meanwhile ZP gives a measure of this stability with the magnitude of its charge, being negative or positive. Unstable solutions possess a ZP value closed to zero and vice versa.

The influence of surface adjustment with a silane agent coupled on $TiO_2$ NPs surface was studied by Zhao et al. [81]. They observed that the isoelectric point (IEP) of the modified $TiO_2$ NPs was changed from pH 6.4 to pH 9.4 after surface modification, and the ZP plateaus rose considerably, which was explained by the protonation of $NH_2$ groups in the acidic area. The considerable reduction in particle hydrodynamic diameters and polydispersity index (PDI) suggested that an increase in particle ZP had a beneficial effect on particle dispersion stability. Oseh et al. [82] modified the surface of $SiO_2$ with APTES and concluded that the modified particles demonstrated strong stability at a higher temperature of 150 °C, implying long-term stability in high-temperature environments. In another report, the ZP values indicated a considerable adsorption and attachment of CTAB molecules on NP surfaces because of the electro-statal interaction between the interacting microbes. However, in the presence of surfactants, the stability of many of these NPs is usually dictated by their charges as well as the concentration of NPs suspended. [83].

### 3.2. Temperature

A lot of research has been carried out on the effect of temperature on NPs synthesis [84-86]. It has been observed that the reaction's bath temperature influences reaction rates, which might lead to the change in morphology of NPs during synthesis [84,85].

Despite the fact that little research has been done on the influence of temperature on NP surface modification, it plays an important part in the process. Most surface modifications processes of NPs have been carried out at ambient temperature whereas bond formation is influenced by temperature, although high temperatures can also cause bond cleavage, in which the material loses its original characteristics. Since NPs have fewer connections with surrounding atoms than bulk particles, thermal vibrations are more likely to disturb the crystal lattice's regular order. Surface modification of NPs must therefore be handled in a controlled temperature range, good enough just to initiate the bonding process with the grafting molecules without leading to further change in the original structure of the particles. Besides, further studies on the influence of temperature on NPs surface modification is a topic of concern. Temperature has an effect on the efficiency of the APTES bonding process, according to Campelj et al, [87]. They equally discovered that the grafting processes of APTES-modified NPs were substantially slower at room temperature than at 50 °C, and that increasing the temperature beyond this point, did not improve the surface amine concentration. Sodipo and Aziz [88] equally reported that, the combined heating and stirring strategy has shown to be the most efficient way of grafting APTES onto the surface of iron oxide NPs. Nonetheless, more work sill needs to be done on the effect of temperature on NPs surface modification.

### 3.3. Ionic strength

To improve NP solution stability by surface modification, a variety of capping agents, including polymers and surfactants, have been extensively explored. Increases in cation valence have also been found to have a substantial influence on the suspension stability of NPs in numerous studies [89]. Steric and electrostatic repulsion both contribute to the stability effect. Ionic species-specific surface adsorption is another important element that influences suspension stability [90]. The adsorption of an uncharged

substance on the NP surface inhibits particle aggregation by steric repulsion, resulting in steric stability. Previous research has shown that Na$^+$ adsorption lowered the point of zero charge (pHPZC) for crystalline anatase TiO$_2$ NPs at low pH [91]. The critical deposition concentration of fullerene (C$_{60}$) NPs was decreased from 120 to 4.8 mM in a research by Chen et al. [92], owing to an increase in the cation valence (Na$^+$ and Ca$^{2+}$, respectively). They then concluded that the surface adsorption of ionic species is an important element that influences suspension stability. High ionic strengths influence the aggregation effect of NPs through the diffuse double layer (DDL). The DDL spreads further away from the surface of the particle at low ionic strengths, promoting particle–particle repulsions. Nevertheless, at elevated ionic strengths, the NP DDL is squeezed and neutralised, resulting in van der Waals aggregation [93].

*3.4. NP surface chemistry*

Amalgamation of other substances onto the surfaces of NPs without jeopardising colloidal stability during the modification process is a common problem of NP functionalization irrespective of the ligand used [93]. The ligand exchange mechanism has received a lot of attention, and it is extremely reliant on the NPs composition [94,95]. As a result, several methods based on the affinity of the surface for different chemical functional groups have been devised depending on the NPs surface nature:

(a) Thiols or, to a lesser extent, amines and cyanides are used to functionalize noble metals such as gold (Au) and silver (Ag), which are also plasmonic materials.
(b) Iron oxides, for example, can be easily coated by forming oxygen bonds with hydroxyl and acidic groups.
(c) Binary compounds, especially those containing elements from groups 12 to 16 of the periodic table, can be easily covered by oxygen bonding with acidic and hydroxyl groups, as components of fluorite.

Many distinct functional groups can be covalently bonded to the NPs surfaces using bifunctionalized thiol compounds [96]. The inclusion of stabilisers and/or surfactants in NPs dispersions may interfere with the formation of Au–S bonds in the case of Au particles. For example, it can reduce reaction yield and hence the reliability and repeatability of the functionalization process [97]. Kockmann et al. [98] tune the surface chemistry of zirconia NPs with extended aliphatic as well as aromatic organic moieties by using a grafting-through method to connect ligands with polymerizable terminal double bonds. In this case, the saturated ligands were employed as unreactive modifications for comparison. It was also discovered that particle modification with a strong affinity and chemical similarity to the polystyrene matrix had a higher mechanical stability. As a result, it is necessary to carefully analyse the potential influence on NPs surface chemistry as an effect of the various procedures and manipulations carried out during the functionalization of NPs in solution [119]. Particle retention, wettability changes, and the ability to emulsify and stabilise emulsions or foams are all determined by particle surface chemistry. The intrinsic surface property is determined by pristine material characteristics; however, material surface attributes may be modified with suitable surface modification. Particle hydrophobicity can be changed by well-designed surface modifications, reducing particle retention on the rock surface [99].

The factors mentioned above are unique to each NP type and surface modification method. Their impact is determined by the type of NP, surface modification method, surface modified agent, and end application. As a result, a specific factor will influence a specific reaction in a specific way. Therefore, the effect of influencing parameters such as temperature, pH, ZP, surface chemistry and ionic strength on Np type and surface modification technique, is an area of interest in further research.

## 4. Effect of NPs surface modification on EOR mechanisms

The ability of nanofluids to improve EOR mechanism under reservoir conditions strongly depend on particle characteristics such, surface charge, particle sizes, surface coatings and ionic interactions among others. These properties are strongly influenced by surface modification which in turn influence their EOR mechanism. For instance, one of the most important topics to address before injecting nanofluids into porous media is the stability of the dispersed NPs. The nanofluids' stability is thought to be a necessity for the NPs' success during fluid injection [100]. The potential difference between the bulk fluid and the stationary layer of fluid connected to the NPs is known as ZP. Low ZP nanofluids cause rapid sedimentation of NPs due to aggregation and agglomeration, whereas high ZP nanofluids depict an electrically stable suspension system [101]. The balance of gravity forces, van der Waals attractive interactions, and electrical repulsive forces is thought to be responsible for the stability of suspending NPs in fluids. If the gravitational and van der Waals attractive interactions between the particles are larger than the electrical repulsive forces, the particles will aggregate and settle [104,105] [301]. One of the driving forces for extracting oil from a rock's pore region is structural disjoining pressure. The structure of the NP enhances the disjoining pressure in the NP wedge film during nanoflooding, with higher pressure around the wedge tip than the leftover of the meniscus (Fig. 4c). In the discontinuous phase, such as oil, gas, or polymer, NPs in an aqueous dispersion tend to form a self-assembled structural array. Particles in the three-phase contact zone can form a wedge-like structure that allows them to press their way between the discontinuous phase and the rock surface. The disjoining pressure force is created when particles in the bulk fluid constantly push particles in the restricted region forward [104,105]. The energy that drives this process include electrostatic repulsion and Brownian motion among the particles. The magnitude of the disjoining pressure is affected by the size of the NPs, the temperature, and the salinity of the base fluid. Furthermore, while the force of a single particle is rather moderate, when a large number of small particles are present, the force at the vertex can reach 50,000 Pa [106]. As a result, the system's equilibrium is disrupted by the disjoining pressure. In order for the system to regain its equilibrium, certain of the system's properties, such as IFT and wettability, would be altered, and oil displacement would occur. [107,108]. The surface modification of NPs influences the disjoining pressure by lowering the sticking effect (agglomeration), which aids the spreading process of NPs.

To separate the oil drop from the pore throat, the nanofluid-oil interface transit cuts through the oil-solid contact [83,109]. The gap between NPs and fluids can be overcome by covering the NPs with a surfactant or polymer [105]. As a result, the particles will be unable to attract one another or surrounding molecules, enabling for stability to be achieved [110]. IFT reduction and wettability alteration were noted to be influenced by surface modification of the NPs [105,111,112]. This is due to adsorption capacity of the particles at the oil water interface [105]. Furthermore, nanofluid properties such as stability, solubility of fluids, mobility, emulsion and foams in porous media can be enhanced by polymer/surfactant coating on the surface of the NPs [105,111,113,114]. Previous studies have reported that coating SiO$_2$ NPs with a surfactant/polymer has proven to be effective for EOR [1,107,110,115-117].

## 4.1. Ift

IFT is one of the key parameters used to assess the flow and motion of fluids in porous media. Thus, it has an effective influence on the reservoir performance in hydrocarbon production [110]. Consequently, determining the IFT between oil/brine or oil/injected fluids is critical in EOR [118]. It is important to have a high capillary number and a low IFT between water and oil to minimise residual oil saturation [110,118].

The capillary pressure, permeability, and flow behaviour of fluids in porous media are directly affected by IFT reduction between oil and water (O/W). NP adsorption at the O/W interface, can significantly decreased IFT, and a higher oil recovery factor could be achieved [201]. Even though NPs have been widely used to decrease IFT several studies have shown the efficacy of surface functionalization of NPs in reducing IFT to ultralow values. The adsorption of NPs on rock surfaces with improved stability due to surface modification can lower the IFT between the rock surface and the oil, disrupting any molecular connection between the rock surface and the oil molecules adhering to it (Fig. 6a). In addition, NPs can adsorb on the O/W interface, lowering the IFT between the two phases. The modified NPs do this by forming a monolayer that substitutes the current O/W interface, serves as a mechanical barrier, and connects the two phases [120-122]. Zargartalebi et al. [123] found that modifying hydrophilic $SiO_2$ NPs with sodium dodecyl sulphate (SDS) reduced IFT and increased oil recovery. They modified $SiO_2$ NPs with two separate internal olefin sulfonates (IOS20–24 and IOS19–23) and discovered that adding a surface modified $SiO_2$ nanofluid reduced the O/W IFT [124]. The result of surface-adjustment on the morphology and size of $SiO_2$ NPs, in addition to IFT reduction, was carried out using 99 % ethanol and TEOS on three forms of silica ($SiO_2$) NPs, including bare-SiO2, TX-100/SiO2, and PEGylated SiO2 [103]. They reported that the TX-100 coated $SiO_2$ NPs produced the lowest IFT value of 7.06 mNm-[1].

IFT is significantly decreased as a result of the inclusion of $SiO_2$ NPs at the interfacial layers to SDS, which improves the efficacy of surfactants in reducing IFT [125]. A research was conducted on the use of two separate surfactants, SDS and CTAB, with the inclusion of $ZrO_2$NP, and the findings showed that the use of NPs allowed for a 70 and 81% reduction in IFT when used in conjunction with SDS and CTAB, respectively [125]. For all the NPs studied, the inclusion

of a benzene ring in the structure of Triton X-100 and SDBS increased their dispersing ability. At 80 °C, electrostatic attraction between the charges on $Al_2O_3$, CuO, $TiO_2$, ZnO, and $ZrO_2$ surfaces and surfactant head-groups resulted in a significant reduction in n-decane-water IFT [66]. In terms of IFT reduction between brine and oil, the effect of functionalized NPs on IFT reduction reported in several studies shows that surface modified NPs are better than unmodified.

## 4.2. Wettability alteration

Wettability is a major factor in increasing fluid displacement performance in porous media. Wettability is described as a fluid's propensity to spread on or conform to a solid surface in the presence of other immiscible liquids. As a result, it has a major effect on oil recovery processes and reservoir efficiency [110]. Moreover, NPs can change the wettability of the rock by removing carboxylic particles in the rock layer, resulting in a wedge film that displaces oil droplets from the rock surface due to disjoining pressure. The pressure necessary to remove fluids that are in contact with reservoir rocks due to the adhesion force of fluids/solid surface is known as disjoining pressure [126]. Theoretical and practical studies reveal that nanofluids diminish oil adsorption on a rock surface by forming a wedge film structure on the rock surface by creating a structural disjoining force (film) between the oil and the rock surface. The tendency for NPs to reorganise in the nanofluid, resulting in an increase in the entropy of the nanofluids, is due to the NPs' significant freedom in the nanofluids. The removal of the fluids originally adhered to the rock leads to wettability alteration.

Besides the use of bare NPs to alter the rocks' wettability and improve oil recovery [102,103], the surface modification of NPs has yielded excellent results in altering wettability. The surface modification of NPs, enhances their surface charge which is a measure of NPs stability. The adsorption of charged NPs can modify the reservoir's wetting characteristics by establishing hydrogen bonds with water molecules, drawing the molecules to the rock surface while lifting oil off it [122] (Fig. 4d). Adil et al. [127] explored the effect of $SiO_2$ nanofluid on the wettability of treated (oil-wet) glass surfaces. They found that the contact angle of $SiO_2$ /TX-100 nanofluid wettability decreased from 130.4° to 78°, indicating a rapid shift in the wettability of the glass surface from oil-wet to water-wet. 0.1 wt% bare $SiO_2$ and $SiO_2$ /PEG nanofluids gave contact angle
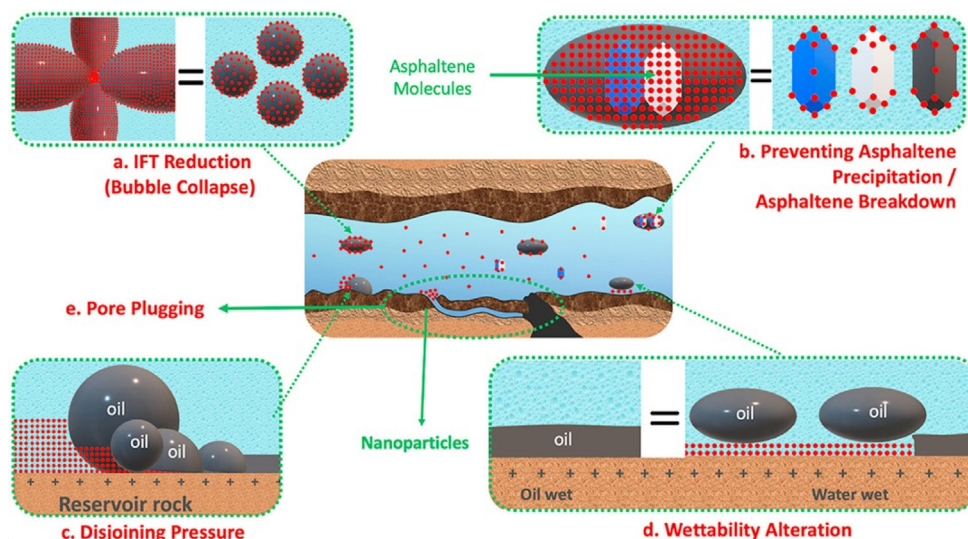


**Fig. 6.** Schematic illustration of various nanofluids oil recovery mechanism. (a) Reduction in IFT (b) asphaltene precipitation and breakdown prevention (c) disjoining pressure (d) wettability change (e) pore blocking) [109].

of 100° and 86°, respectively. After soaking in various concentrations of SiO$_2$ nanofluid, the contact angle of the treated glass surface indicates a substantial change in wettability with increasing NPs content. The transition in water wetness of the glass surface from oil-wet to water-wet was attributed to the even and actual dispersion of spherical TX-100/SiO$_2$ NPs, which offers increased interaction with crude oil components as well as the solid surface. In another report, the glass surface was saturated with surfactant-coated SiO$_2$ nanofluids, the contact angle between glass slides and IOS-modified silica was found to decrease significantly from 80° to the least values of 3°–2° in an experiment by Ahmed et al. [124]. The decrease in contact angle when the SiO$_2$ nanofluid was added meant that all surface-coated SiO$_2$ nanofluids could change the rock wettability toward firmly water-wet. Ngouangna et al. [1] used APTES to modify the surface of SiO$_2$ NP, they reported that the NP modified with APTES changed the contact angle of a sandstone core from oil wet to water wet. According to the findings, surface modified NPs can reduce CA to significantly lower levels than unmodified NPs. The extent of CA reduction, on the other hand, is totally dependent on the type of NP, surface modification process, oil properties, rock properties, and reaction medium (reservoir conditions).

### 4.3. Mobility control and viscosity

One of the most fundamental principles in any EOR process is mobility control. It can be accomplished by injecting chemicals to increase the viscosity of displacing fluids. The displacing fluid mobility must be equal to or less than the mobility of displaced fluids [128] (Equation 1). Several factors must be considered before fluid injection, including flow rate, permeability, reservoir thickness, and fluid density. By lowering the viscous force of the crude oil or increasing the viscosity of the injected fluids, the mobility ratio can be lowered. [129]. Due to special forces (viscous, gravitational, and capillary) exerted on the oil ganglion after water floods, a considerable portion of the oil is often caught in the reservoir rock pores, inhibiting the oil's effective mobility. Therefore, the solid attraction of such forces on oil must be monitored in order to achieve or accomplish oil recovery, which may be accomplished in stages using various NPs, [129,130].

$$M = \frac{\lambda i}{\lambda o} = \frac{Kri/\mu i}{Kro/\mu o} = \frac{Kri\mu o}{Kro\mu i} \qquad (1)$$

where $\lambda i$ and $\lambda o$ denote mobility of the fluids injected and oil, separately, $Kri$ is relative permeability of the fluid injected, $Kro$ is the oil's relative permeability, and $\mu o$ and $\mu i$ the viscosity of the oil and injected fluids.

To avoid viscous fingering, a mobility ratio of less than one is preferable. The increased mobility of water causes viscous fingering in the case of a higher mobility ratio. Rheology is a useful tool for determining the viscosity of injection fluids [131]. The mobility ratio (Equation 1), which is the ratio of the displacing fluid to the displaced fluid, is therefore a significant dimensionless number in EOR. For more oil displacement, a low mobility ratio ($\leq 1$) is required, which results in a higher sweep efficiency and less fingering effect in the reservoir [99].

Although several NPs have been extensively accessed for oil mobility control, surface adjusted NPs have proven to yield better results. In a report, using nano-SiO$_2$ and free radical polymerization to create a new polymer nanocomposite for use in a polymer flooding process. Under different conditions, oil displacement performance, mobility control capacity, salt tolerance, temperature tolerance, viscoelasticity, and rheological properties were tested. The experimental findings showed that polymer nanocomposite has excellent mobility regulation, temperature resistance, and rhe-

ological properties for polymer flooding as a chemical agent [132-134]. In another study, a polymer was used to functionalize SiO$_2$ for use in EOR. They pointed out that extra energy was needed for the nanofluids to mobilise the trapped oil. Physicochemical interactions between NPs and the rock system, deformation and breakage of oil and/or NPs blocking enough pores to build up enough pressure inside the pores to detach and mobilise the oil in neighbouring pores all contributed to this energy. They went on to say that polymer functionalized SiO$_2$ NPs would effectively improve EOR [120]. Ahmed et al. [124] used HPHT modular Compact Rheometer (MCR 302) to test the rheological properties of SiO$_2$ treated with surfactant. The DG 26.7 double-gap geometry was used to obtain measurements at room temperature. At different shear speeds (0–100 s$^{-1}$), the viscosities of 0.10 wt% (1000 ppm) nanofluids (clean silica NP solution, Surf X- and Surf Y-coated NP solutions) were tested. After an exponential drop (30 s$^{-1}$), the viscosity of the Surf Y-coated silica nanofluid reached a plateau (greater than 30 s$^{-1}$). The Surf Y-coated silica nanofluid's behaviour makes it suited for EOR applications that require a stable displacement front. The viscosity of the Surf X-coated silica nanofluid, on the other hand, increased after shear rates greater than 85 s$^{-1}$, which could be attributed to particle aggregation at high shear rates. The results therefore confirmed that IOS$_{(0-24)}$ is the most suited for coating SiO$_2$ in EOR applications. Despite the benefits of surface modified NPs in raising viscosity, polymers are still the most used viscosity-enhancing agents. Modified NPs, on the other hand, may be preferred because of the additional benefits they provide, such as IFT decrease, wettability modification, and emulsion stability.

### 4.4. Asphaltene precipitation

In numerous literatures, the terms "precipitation" and "deposition" have been used interchangeably to describe the process by which asphaltene molecules exit the oil phase as a detached solid particle [135]. Asphaltene precipitation can occur throughout all the stages of crude oil recovery which might reduce production efficiency. According to Feng et al. [136] there are four types of formation change caused by asphaltene deposition: (1) physical obstruction or permeability reduction, (2) wettability change, (3) crude oil viscosity decrease, or (4) creation of a water-in oil emulsion. The initial phase in asphaltene deposition is the adsorption of asphaltene molecules on the surface of the rock which is followed by hydrodynamic retention and/or entrapment of the particles at the pore throat, finally resulting in a reduction in effective hydrocarbon mobility [137].

Physical obstruction, appears to be the most common cause of formation damage. The first phase in asphaltene deposition is adsorption of asphaltene molecules on the rock surface, which is followed by hydrodynamic retention and/or trapping of the particles at the pore throat, resulting in a reduction in effective hydrocarbon mobility [138].

Reservoir wettability is a crucial concept in reservoir engineering, and it has been the subject of numerous researches over the years due to its significant impact on production capacity. Changes in the pore system (adsorption) have been linked to wettability changes, which can be caused by rock–fluid interactions, fluid–fluid interactions, rock mineralogy, and brine chemistry. Asphaltene can compartmentalise a reservoir at the reservoir size, but at the pore scale, it can build flow barriers, change the relative permeability and wettability of the rock, and so affect ultimate recovery [139]. Asphaltenes tend to precipitate in non-uniform patterns on rock surfaces, depending on pore geometry, surface roughness, and mineralogy. These can cause the rock's wettability to shift completely or partially [139]. A strong interfacial boundary condition exists within the rock system, making a fluid preferentially

mobile in the presence of other fluids, which determines a reservoir's wettability. As a result, it is mostly owing to the pore structure being adhered to or coated with a fluid that is either hydrophobic or hydrophilic. The adsorption of fluids onto the rock, on the other hand, is influenced by a variety of circumstances, including well operations and interactions [140]. Due to electrochemical interactions, asphaltene adsorbs on the pore surface, covering the surface and modifying the wettability.

The influence of asphaltene content on the viscosity of heavy oils has been investigated for a long time. The largest molecular weight component of crude oil is asphaltenes. They are fractions that are insoluble in pentane or heptane and contribute to the viscosity of heavy oil. As a result, one of the most effective ways to reduce oil viscosity is to remove asphaltene [141]. In the meantime, the chemical structure of the precipitated fractions is clearly influenced by the solvent used. From a practical standpoint, this may not be critical. Even the grouping of thousands of chemicals into a single category known as "asphaltenes" is based solely on practical considerations. The average molecular weights of the precipitated asphaltenes are clearly different [142]. Accordingly, they have varied effects on the rheological properties of their solutions. The asphaltene solutions can be diluted or concentrated, and the crossover concentration rises as the amount of asphaltenes in crude oil rises. Asphaltenes precipitated at lower levels have a propensity to increase the viscosity of solutions of the same concentration. Because of the glass transition of asphaltene, increasing the asphaltene concentration in tetralin (as a model system) results in a change from Newtonian fluid to viscoelastic shear-thinning liquid to gel system [143]. The more asphaltenes are removed from heavy oil, the greater the reduction in viscosity accomplished by deasphalting. Especially at low temperatures, the viscosity drop can be rather dramatic (by tens or hundreds of times). The choice of a precipitant, which gives a mechanism of modulating viscosity, determines the efficacy of asphaltene removal.

The precipitation of asphaltenes in both upstream and downstream oil industry facilities has been connected to a slew of issues. Natural emulsifiers such as asphaltenes in the oil reservoir are expected to have a major role in the production of crude emulsions [142]. Several studies have stressed on the importance of asphaltene in stabilising crude emulsions and propose the idea that asphaltenes could possibly adsorb on reservoir minerals and contribute to emulsion stability [144]. Crudes having a higher potential for asphaltene precipitation, according to Kokal and Al-Dokhi, [145] are more likely to generate kinetically stable emulsions.

Asphaltene precipitation and deposition can be reduced via nanofluid flooding by the adsorption of the molecules. NPs operate as an inhibitor, preventing the precipitation of crude oil asphaltene [135]. They encircle and degrade asphaltene molecules, lowering viscosity and inhibiting deposition, precipitation, and aggregation, on the rock surface (Fig. 4b).

The adsorption of asphaltene onto $SiO_2$ NPs, both in their natural state and with surface changes, was investigated. The results demonstrated that surface modification improved the adsorptive capabilities of NP. The extent of the enhancement was significantly influenced by the molecular characteristics of the capping molecules [146]. The effects of amino functionalised carbon NPs (CNPs) on asphaltene precipitation and aggregation in an unstable crude oil were investigated. The study discovered that CNPs effectively delayed asphaltene precipitation in a variety of studies and simulations, proving the inhibitory action of CNPs against asphaltene production. Apart from the asphaltene inhibitor activity, CNPs absorbed asphaltenes and caused a slower asphaltene aggregation process, resulting in a narrower size range of asphaltene aggregates and good stability [147]. Vineet, [148] in his report highlighted that, compared to adsorption on pure $SiO_2$ the adsorption

of asphaltene and polymer clusters was decreased by more than half after applying a surfactant and a silane layer. Despite the fact that the hexadecyl trimethyl ammonium bromide (HTAB) (16 carbon atoms) and octadecyltrichlorosilane (OTS) (18 carbon atoms) hydrophobized the $SiO_2$ particles to the same extent, surface imperfections and weak bonding allowed the HTAB pre-adsorbed $SiO_2$ to adsorb asphaltenes more than the silane functionalized $SiO_2$. Thus, the hydrophobicity of the silanes has no bearing on the reduced adsorption rather, it is the ability of the surfactant monomers and silanes to shield the underlying silanol groups that aided the reduction of adsorption.

## 4.5. Foam

Foam can restrict gas mobility by raising the drag force of moving bubbles on the porous walls and by catching a substantial gas component in the pore media through raising the viscosity of apparent gas and lowering relative permeability of gas [149]. Surfactants have been used as a foam production agent in experimental investigations to minimise gas mobility in gas flooding [150]. Traditional surfactant foam flooding is often challenged by harsh environments, such as high temperature, high pressure, and high salinity, because molecular surfactant can undergo phase separation and make the surfactant solution into inhomogeneous phases [99]. Surface-modified NP, on the other hand, have been stated to have high thermal stability and have been studied in the laboratory using flooding experiments. The synergistic effect of surfactant and NPs, or the modification of the surface of solid NPs via physiochemical interactions with surfactants, may improve foam stability and produce stronger foams than surfactants alone [151,152]. Surfactant-stabilized foam fluids with NPs improve the mechanical barrier (electrical repulsive + steric) surrounding bubble/oil interfaces, reducing the potential for foam film to coalesce [153]. Singh and Mohanty [154] demonstrated synergistic stabilisation of nitrogen-in-water foams by combining surface modified $SiO_2$ NPs and anionic surfactants. They highlighted that the foam mobility reduction factor in Berea sandstone core rose as the degree of surface coated NPs increased. Furthermore, foam can be stabilised in porous media by in situ surface activation of NPs, and they have the ability to operate as surfactants, according to their foam flow investigations [154].

Several studies have found that surfactant-NPs mixtures can improve foam stability. The key parameters influencing NPs stabilised foam are the kinds of NPs used, NP modifiers, salinity, temperature, and the concentration ratio of NPs to surfactant [155,156]. NPs have a greater thermal stability and have been extensively tested for foam stabilisation [197]. Previous research has shown that super-stable foams are formed by partly hydrophobic NPs with contact angles ranging from 60° to 100° [83].

Sun et al. [157] explored the synergistic foam stabilisation mechanism with surfactants and the rheological features of the gas–liquid interface by introducing modified hydrophobic $SiO_2$ NPs into the foam system. They discovered that the surfactant molecules were adsorbed at the right concentration onto the particle surfaces. They further explained that the particle's surface activity can be increased, which aids in particle adsorption at the gas–liquid interface and affects the structure of the particle's interface layer, improving the foam's expansion viscoelastic modulus and stability. ShamsiJazeyi et al. [158] investigated the influence of partly hydrophobic polymer-modified $SiO_2$ NPs on foam flow in the Boise sandstone and discovered that the presence of partly hydrophobic polymer-modified $SiO_2$ NPs enhanced the flow pressure drop. Risal et al. [83] investigated the stability of surface modified $SiO_2$ NPs on foam and noticed that the inclusion of surface modified $SiO_2$ NPs significantly improved foam stability. They also observed that better foam stability was demonstrated by increased

plugging pressure. Binks et al. [159] created a strong foam by combining calcium carbonate (CaCO$_3$) NPs and the surfactant sodium stearoyl lactylate.

### 4.6. Emulsion

Nanoemulsions, often known as "smart fluids," are droplet sizes ranging from 10 to 500 nm, homogenously mixed immiscible liquids. They are distinguished from macroemulsions with droplet sizes ranging from 1 to 100 mm by their exclusive physical and chemical traits of ultralow IFT, tiny size of droplet, and lasting stability owing to Brownian motion of the droplets on a continuous basis [135,160-162]. The use of a surfactant and NPs mixture for emulsion stabilisation is an exciting area of research since the properties of the emulsion generated will be determined by the synergic interaction between particle and surfactant at the emulsion droplet interface [163]. Oil, water, and emulsifier(s) that function via electrostatic interactions and/or steric hindrance are the main components of nanoemulsion systems [164]. The most common kind of emulsion at the nano-scale is oil in water emulsion, in which droplets of oil are spread in a continuous aqueous phase. On the other hand, water in oil emulsion is another type of emulsion in which dewdrops of water are scattered throughout the continuous watery oil phase. Whereas in a bi-continuous nanoemulsion, oil and water microdomains are interspersed throughout the system [160]. The lack of shear-thickening and sedimentation problems in nanoemulsions make them appealing for EOR applications. Nanoemulsion droplets are resistant to sedimentation and creaming kinetically [161]. Nanoemulsions and microemulsions have considerable distinctions. The former are thermodynamically unstable systems that require energy to be created, whereas the latter are thermodynamically stable [161,165]. The development of emulsions is mostly determined by the makeup of crude oil, particularly the levels of gelatine and asphaltene [166]. The saturation of the non-wetting phase is lowered when the viscosity reaches a predetermined threshold. The non-wetting phase becomes discontinuous, disperses in a continuous wetting phase, and flows as an oil droplet or emulsion [167]. The mechanisms governing the formation of emulsion is termed the snap-off process (Fig. 7a), which

is contingent on the velocity, viscosity ratio, capillary number and pore-throat ratio [168]. Hoyer et al. [169] observed the snap-off drops in a constricted capillary with an elastic interface, implying that the rheology of the interface has a significant impact on a suitable viscoelastic behaviour at the interface may lead to excellent interfacial stability against snapping.

NP-stabilized emulsions are said to be extremely stable, allowing them to withstand severe reservoir conditions. Thus, water channels fingered across a water-flooded reservoir can be more effectively blocked by emulsion droplets stabilised by NPs, resulting in more persistent flow divergence. Oil entrainment in the form of oil in water emulsions has been proposed as another emulsification assisted EOR mechanism in addition to channel plugging [170]. Though numerous researches have been carried out on the use of NPs to stabilize emulsion, surface modified NPs have proven to be more efficient. Recent studies have equally proven that highly hydrophilic SiO$_2$ NPs do not adsorb at the oil–water interface and must be surface activated in order to function as emulsifiers and has equally been proven successful in oil field applications [170]. The attachment of the particles to the droplet surfaces is the mechanism of NPs stability (Fig. 6b). Using non-modified and functionalized NPs obtained following deep eutectic solvent (DES) pretreatments, Ojala et al. [172] investigated the influence of morphology and surface characteristics of cellulosic NPs that is CNC and cellulose nanofibers (CNFs) on O/W emulsion stabilisation. According to their findings, all cellulose-NP stabilised emulsions developed creaming layers, although the creaming kinetics varied depending on the kind of NP used, as evidenced by the stability study. Creaming prevention was shown to be most effective with functionalized SF-CNFs. Furthermore, the oil droplets were stable against coalescence when SF-CNFs were used. Sharma et al. [171] utilised lubricating oil, polymer polyacrylamide (PAM), SDS, and NPs such as silica, clay, and copper oxide to create a new O/W emulsion stabilised by a NP-surfactant-polymer system. The thermal stability of this pickering emulsion was investigated, and the results revealed greater thermal stability than emulsions stabilised using a surfactant-polymer combination, and that hydrophobic clay NPs and salt (NaCl) can improve the thermal stability of pickering emulsions to some extent. Table 3 summarises previous
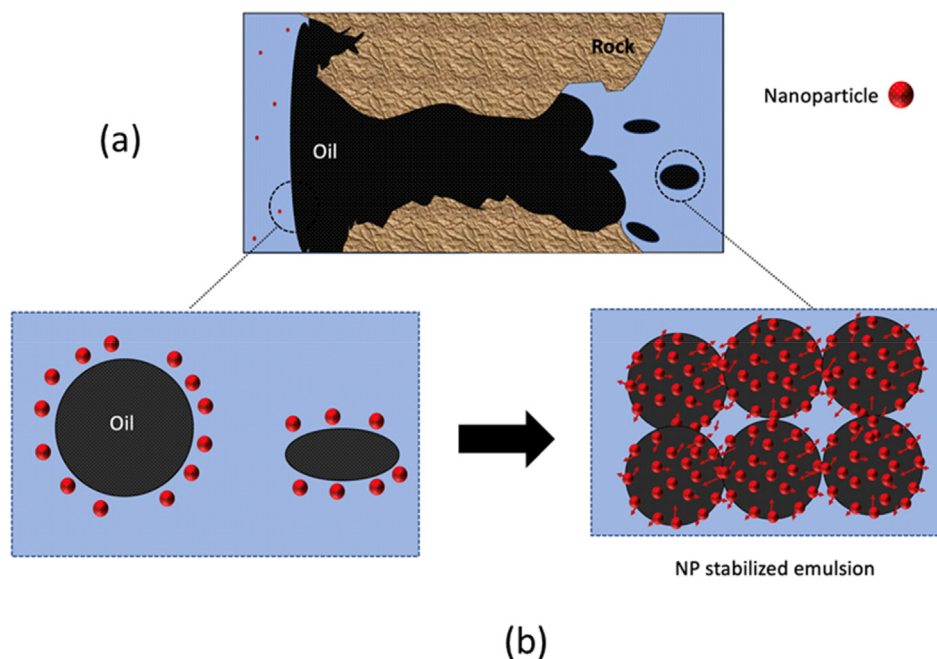


**Fig. 7.** (a) Emulsion formed by the snap-off process and (b) NPs stabilizing Emulsion.

**Table 2**
Summary of previous work using surface modified NPs on EOR Mechanisms.

| Modified NP/ Material used | NP Concentration | Findings | EOR Mechanism | Method Used in Findings | Reference |
|---|---|---|---|---|---|
| Cobalt ferrite/ DBSA | 0.1 wt% | Decrease in asphaltene precipitation | Asphaltene Precipitation | UV–Vis spectrometry | Oliveira et al. [174] |
| ZrO$_2$/SDS & CTAB | 0.001 – 0.05 wt% | Change in IFT from 71.2 − 36.8 mN/m | IFT reduction | Pendant Drop | Esmaeilizadeh et al. [175] |
| SiO$_2$/SDS | 1.0 wt% | Change in IFT from 20 to 1.87mN/m | IFT reduction | Spinning Drop | Zargartalebi et al. [176] |
| ZrO$_2$/SDS | 0.05 wt% | IFT reduction from 8.46 to 1.85 mN/m | IFT reduction | Ring | Moslan et al. [177] |
| SiO$_2$/alcohol ethoxylate | 1.0 wt% | Enhanced foam stability and viscosity | Foam stability and viscosity enhancement | Foam generation in test tubes | Alyousef et al. [178] |
| SiO$_2$/PEG | 0.02 wt% | Enhancement in adsorptive properties of asphaltene | Asphaltene precipitation | Batch Adsorption | Vargas et al. [179] |
| SiO$_2$/IOS | 0.3 wt% | IFT reduction from 17.1 to 6.0 mN/m | IFT reduction | Spinning Drop | Ahmed et al. [180] |
| SiO$_2$/APTES and CTAB | 0.05 wt% | Reduction in IFT from 17 to 2.28 mN/m | IFT reduction | Ring | Wu et al. [181] |
| SiO$_2$/IOS | 0.05 wt% | 80 – 3–2 ° reduction in contact angle | Wettability alteration | DIW/glass slides | Ahmed et al. [180] |
| CaCO$_3$/MMTS | 15 wt% | O/W emulsifier and a powerful foam stabiliser | Foam stability | Fluorescence microscopy | Lee et al. [182] |
| SiO$_2$/PTMS | 1.0 wt% | Emulsion modulation in the presence of hydrophobic NPs | Emulsion formation | Emulsions formed with the use of n-hexane | Ghaleh et al. [183] |
| SiO$_2$/TX-100 | 0.1 wt% | 14.3 – 10.2 & 8.15 mN/m & Contact angle reduction from 130.4 to 78 ° | IFT reduction, Wettability alteration | Spinning Drop, Brine/glass slides | Adil et al. [184] |
| SiO$_2$/APTES | 0.01 – 0.3 v/v % | Change in IFT from 15.7 to 8.5 mN/m | IFT reduction | Ring | Ngouangna et al. [1] |
| SiO$_2$/CTAB | 1.0 wt% | Improved foam stability | Foam stabilization | Foam produced using N$_2$ gas | Choi et al. [25] |
| SiO$_2$/IOS | 0.1 wt% | With increased shear strain, the viscosity of nanofluids decreases. | Improved fluid viscosity | HPHT Modular Compact Rheometer | Ahmed et al. [180] |
| SiO$_2$/ Polyethylene glycole | 5 wt% | Reduction in contact angle from 62 − 23 | Wettability alteration and reduction in oil viscosity | Glass beads | Daneshmand et al. [185] |
| SiO$_2$/Polymer Al$_2$O$_3$/ Polymer | 0.02 wt% | IFT reduction, Contact angle reduction, viscosity increase | IFT reduction, Wettability alteration Fluid viscosity improvement | Glass Beads | Hu et al. [186] |

research on the effect of surface modification of NP on EOR mechanisms.

## 5. Applications of surface modified NPs in EOR

NPs have piqued the interest of researchers in the upstream petroleum sector for oil recovery applications, thanks to their large surface-area and increased chemical reactivity. In oil–water–solid contact area, NPs adsorb on the rock surface and create a wedge film. When the disjoining pressure is greater than the oil droplet adhesion, the wedge film provides a structural disjoining pressure that causes oil droplets to be removed from the rock surface. The usage of surface-functionalized NPs to improve reservoir rock and fluid characteristics under specific reservoir circumstances has proven to improve oil recovery during EOR processes in numerous studies. The flooding capability of modified carbon NPs was investigated by Kanj et al. [87]. They reported that carbon-based fluorescent NPs enhanced the oil recovery factor in carbonate reservoirs by more than 96%. Zargartalebi et al. [187] reported that hydrophobic NP-modified surfactants surpassed hydrophilic NP-modified surfactants in terms of efficiency. The release of oil droplets in the reservoir during EOR applications is caused by a mixture of surfactants and NPs, which are trapped in the reservoir rock's narrow throats and microchannels. These occurrences are linked to several factors that contribute to increased oil recovery, including reservoir rock wettability, spontaneous emulsion formation, varying IFT between reservoir fluids, and porous media flow characteristics [132,188]. Surface modified NPs can also generate a wedge film or structural disjoining pressure, which can sweep

oil droplets away from the rock surface increasing oil recovery [189]. The effect of SiO$_2$ NPs and SDS surfactant using micromodel at 2.2 wt% SiO$_2$ NPs slowed breakthrough and improved sweep performance [190].

Due to their natural abundance silicon dioxide in sandstone formations (99.8%), low cost, physical/chemical modifiability, and environmental friendliness, modified SiO$_2$ NPs are the most frequently used for EOR mechanism [191]. Bila and Torsaeter, [122] examined the use of polymer-coated silica NPs in tertiary flooding for oil recovery at high temperatures and high salinity conditions. They reported up to 6% additional recovery to the OOIP after waterflooding. Choi et al. [192] found that when polymer-coated silica NPs were injected into water-wet core samples, 74.1 % of the oil was extracted, compared to 68.9 % of initial oil in place (OOIP) from water flooding and 72.7 % of OOIP from bare SiO$_2$ NPs. Bila et al. [122] recently evaluated a variety of polymer-functionalized silica NPs and found that after water flooding, the additional oil recovery was 5.2 % of OOIP. The oil recovery, like Choi et al. [192], was due to a decrease in IFT. The reduction in oil/water IFT and the development of a wedge layer between the oil and the rock surface, which affected the wettability, were linked to the processes of oil recovery. Dai et al. [193] investigated the capacity of surface-modified silica NPs to reduce water injection pressure for EOR applications. From their results, scanning electron microscope (SEM) images and contact angle measurements showed that modified SiO$_2$ NPs can be adsorbed on the surface of rocks, converting the rock surface from hydrophilic to hydrophobic. Thereby, greatly lowering the water flow resistance which can have a wide range of uses in the development of oilfields, as it will lower the water-injection

**Table 3**
Summary of the applications of surface modified NPs in EOR.

| NP used/Modifying Agent | NP Concentration | Dispersion Medium | Porous Media/EOR Mechanism | Findings | Reference |
|---|---|---|---|---|---|
| Fluorescent NP | – | – | Carbonate | 96% oil recovered | Kanj et al., [87] |
| SiO$_2$/hexadecyl silane | 10 vol% | Brine | Sandstone// wettability, IFT | Additional oil recovery of 26.2% | Roustaei et al. [205] |
| SiO$_2$/MPEG | 1.0 wt% | Distilled water | Carbonate core/ viscosity | Improve oil recovery from 54% to 59% | Behzadi et al. [196] |
| SiO$_2$/Polymer | – | brine | Wet cores/viscosity | 68.9–74.1 incremental oil recovery | Choi et al. [192,197] |
| ZnO/SDBS | 01.wt. % | Brine | Sand Pack | Additional oil recovery of 8.5 – 10.2% OOIP | Adil et al. [191] |
| Fe$_3$O$_4$/Chitosan | 0.03 wt% | Sea water | Sand Pack/ wettability | 10% increase in oil recovery | Rezvanin et al. [195] |
| SPN/PAM | 0.5 – 0.9 wt% | Brine | Sand Pack/viscosity | 19.28 % OOIP was recovered through the formation of pickering emulsion and disjoining pressure | Khalil et al. [196,197] |
| SiO$_2$/Polymer | 21.6 – 3608% | Distilled water | Berea Sandstone/ viscosity | Incremental oil recovery of 2.6 – 5.2% OOIP | Bila et al. [191] |
| SiO$_2$/SDS | 2.2 wt% | – | 5 spot micromodel/foam, emulsion, IFT | Slowed breakthrough | Rezk and Allam [198] |
| SiO$_2$/KH540 | 0.1 wt% | Distilled water | Sandstone/IFT, emulsion, foam | Improved oil recovery of 26% OOIP | Lai et al. [199] |
| SiO$_2$/APTES/PAM | 0.1 wt% | Brine | Sand Pack/viscosity, wettability | 9.6% improved oil recovery | Haruna et al. [200] |
| SiO$_2$/PAM | 0.1 wt% | Brine | Sand Pack/ viscosity, wettability | 16.2% additional oil recovery | Haruna et al. [200] |
| Fe$_3$O$_4$/PVP & Fe$_3$O$_4$/ SDS | 0.5 wt% | Brine | Carbonate core plugs/IFT, foam, emulsion | PVP and SDS-coated NPs increased oil recovery by 16% and 13%, respectively. | Shalbafan et al. [201] |
| SiO$_2$/IOS | 0.3 wt% | Brine | Sandstone/IFT, foam, emulsion | Improved oil recovery from 9.1% – 21.7% | Ahmed et al. [180] |
| SiO$_2$/APTES | 0.3 v/v % | Brine | Glass beads/ Wettability | Incremental oil recovery from 69% – 75 % of OOIP | Ngouangna et al. [1] |
| SiO$_2$/Polymer | – | High salinity medium | Core plugs/ wettability, viscosity | 6% incremental oil recovery | Bila and Torsaeter [122] |
| SiO$_2$/Polyethylene Glycole | 5 wt% | Brine | Glass beads// wettability, viscosity | Reduction in oil viscosity and contact angle implying good for EOR. | Daneshmand et al. [185] |
| SiO$_2$/Polymer Al$_2$O$_3$/Polymer | 200 mg/L | KCL Brine | Glass beads// wettability, viscosity | 67% oil recovery for SiO$_2$ & 63 % for Al$_2$O$_3$. Improved recovery through wettability alteration, IFT reduction and fluid viscosity increase. | Hu et al. [186] |
| SiO$_2$/polyethylene glycol & diol functionality | 0.1 wt% | Brine | Sandstone// wettability, viscosity, IFT | Improved recovery from 4% – 50 % through IFT reduction and better emulsification | Saleh et al. [202] |

pressure. Ahmed et al. [180] studied IFT reduction in pure and surfactant coated SiO$_2$ nanofluids. They explained that the surface modified SiO$_2$ nanofluids could boost ultimate oil recovery from sandstone cores by 9.1% and 21.7 %, respectively. At a temperature of 25 °C, when compared to employing simply surfactants, nanofluids of 70–150 nm soluble in an aqueous solution of surfactants will boost oil recovery by 35% in a homogeneous reservoir and 17% in a heterogeneous reservoir. As the fluid's properties shift from Newtonian to non-Newtonian, the recovery increases as the IFT decreases [194].

### 5.1. Current Challenges, opportunities and future prospects

The surface modification of NPs methods should be closely related to their application ranging from ceramics, medicine, textiles, cosmetics, agriculture, optics, food packaging, optoelectronic devices, semiconductor devices, aerospace, construction catalysis and EOR applications. There are many approaches for surface alteration currently available, but there are still few avenues to address the problem profoundly, necessitating further study. Despite the fact that the use of surface modified NPs will have major technological benefits, the disadvantages as well as new opportunities cannot be overlooked. In EOR applications, the cost of NP is a vital factor to remember before beginning any project. In general, the

synthesis, service, and processing of NPs may be very costly; additionally, significant NP injection volumes can be expected during the procedures necessitating a thorough investigation on the benefits and drawbacks before the start of the project. Other challenges include:

- Several NP surface modification approaches have been demonstrated to have diverse properties and mechanisms for EOR and other applications. However, no research on the use of nanofluid mixtures. The synergy between two or more nanofluids can enhance the efficiency of the nanofluid.
- Despite the fact that modified NPs increase NF rheology more than unmodified NPs, polymers are still the most used viscosity enhancers. As a result, polymers will always be prioritised for viscosity enhancement.
- Surface modification of NPs at low temperatures has been shown to be successful, but no research has shown that functionalization at high temperatures is unsuccessful. Because of activation energy (energy required to start a chemical reaction), more bonds can be formed at higher temperatures, making the modification process more efficient.
- Economic deliberations must be considered while doing research on the surface modification of NPs and the preparation of stable nanofluids in large quantities.

- In EOR applications, both unmodified and surfaced NPs have been employed widely. Nevertheless, most of the previous research has concentrated on the physical interactions of nanofluids with reservoir fluids. The chemical interactions between nanofluids and reservoir fluids and rocks at various salinities and temperatures may help researchers better understand how NPs improve oil recovery.
- Other significant difficulties include the circumstances and special properties of each oil field, as well as the compatibility of NPs with them. In certain formations, high temperatures, chemical changes, and salinity can be destructive to NP structures. As a result, taking into consideration such conditions before NPs surface modification is a call for concern.
- Although the surface modification of NPs enhances its stability through ZP analysis at varied pH, this is mostly proven at the laboratory scale whereas in EOR applications, the influence of reservoir pH on the stability of the modified NPs still needs attention.
- The majority of NPs used in EOR are hazardous to the environment and humans. To avoid the danger, comprehensive research on the health and safety of NPs is required. Bionanomaterials research could provide a solution to this challenge.
- Despite various reports of NPs-stabilized foam stability investigations, the effects of surface-modified $SiO_2$ NP on dynamic foam stability and pore blocking performance in porous media are still not understood profoundly [203,204]. Most of the current research has focused on bulk foam stability. Hence, more research is required in this area.
- Surface modification of NPs is still in the laboratory stage. There are still no field trials on EOR. However, laboratory results indicate that they have potentials for field applicability. Hence, collaboration between research institutes and oil industry is needed to facilitate field application. Thus, the hydrophobicity of the silanes has no bearing on the reduced adsorption rather, it is the ability of the surfactant monomers and silanes to shield the underlying silanol groups that aided in the reduction of adsorption.
- The application of NPs in EOR mechanisms has been extensively assessed using simulation studies and mathematical modelling. Despite their success in EOR via colloid filtration theory, transport model approaches, and filtration models with site blocking and detachment, little or no work has been done on surface modified NPs. As a result, there is a need for research in this area.
- To better understand the deposition and retention of NPs in porous media, extensive laboratory testing of unmodified and surface modified NPs has been conducted. However, the majority of porous media used to date have been sand packs, glass beads packs, or grinded rock packs, all of which have high permeabilities in comparison to the reservoir permeability. In order to provide a comprehensive image of what happens in the reservoir, the usage of actual core plus need to be evaluated.

## 6. Conclusions

In this review, the Methods, influencing parameters, advances and prospects of surface modification of NPs on oil recovery mechanisms were critically assessed. The impact of surface modification on EOR were discussed in detail. The results show potential applicability and the challenges encountered during surface modification have offered new prospects for research. From the discoveries of this work, the following conclusions were reached.

1. The "grafting from" is preferable for sterically stabilising NPs in a polymer matrix because it allows for higher grafting densities and thus larger polymer coverages of the NP surface. Consequently, it is frequently used in the polymer functionalization of NPs.
2. Surface changes with well-designed surface modifications can decrease particle hydrophilicity, reducing particle retention on the rock surface. As a result, depending on the surface nature of the NPs, numerous approaches based on surface affinity for distinct chemical groups have been devised: Thiols or, to a reduced extent, amines and cyanides are commonly used to functionalize noble metals. Oxides, on the other hand, can easily be covered by forming oxygen bonds with acidic and hydroxyl groups. Binary compounds, on the other hand, can be easily covered by forming oxygen bonds with acidic and hydroxyl groups.
3. The literature reviewed showed that functionalized NPs have excellent mobility regulation, temperature resistance, rheological properties, effective creaming prevention and the oil droplets are stable against coalescence.
4. The snap-off process, which is influenced by velocity, viscosity ratio, capillary number, and pore throat ratio, governs the generation of functionalized NPs emulsion. The rheology of the interface has a considerable impact on the snap-off drops, implying that an acceptable viscoelastic behaviour at the interface could lead to optimal interfacial stability against snapping.
5. The review experimental results indicate that surface modified NPs can further increase oil recovery by 2.6–5.9% OOIP.
6. From the review, we can conclude that there is no single optimum NPs surface modification technique because each modification type is specific to the end application. As a result, all approaches are given equal weight when it comes to specific aims.

## Declaration of Competing Interest

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

## Acknowledgements

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