Journal of Molecular Liquids 312 (2020) 113434

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Review

Dynamics of oil-water interface demulsification using multifunctional magnetic hybrid and assembly materials

Nisar Ali [a,*], Muhammad Bilal [b,*], Adnan Khan [c], Farman Ali [d], Yong Yang [a], Mujeeb Khan [e], Syed Farooq Adil [e], Hafiz M.N. Iqbal [f]

[a] Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, National & Local Joint Engineering Research Center for Deep Utilization Technology of Rock-salt Resource, Faculty of Chemical Engineering, Huaiyin Institute of Technology, Huai'an 223003, China
[b] School of Life Science and Food Engineering, Huaiyin Institute of Technology, Huaian 223003, China
[c] Institute of Chemical Sciences, University of Peshawar, Pakistan
[d] Department of Chemistry, Hazara University, Mansehra 21300, Pakistan
[e] Department of Chemistry, King Saud University, Riyadh 11451, Saudi Arabia
[f] Tecnologico de Monterrey, School of Engineering and Sciences, Campus Monterrey, Ave. Eugenio Garza Sada 2501, CP 64849 Monterrey, Mexico

ARTICLE INFO

Article history:
Received 19 February 2020
Received in revised form 2 May 2020
Accepted 22 May 2020
Available online 25 May 2020

Keywords:
Emulsion
Hybrid materials
Magnetic nanostructures
Wettability
Oil-water separation
Environment impacts
Wastewater treatment

ABSTRACT

Wastewater produced during the petroleum extraction process and the release of large volumes of hydrocarbon-contaminated wastewater by petrochemical industries are of major concern because of their potential impacts on the environments, animals, plants, and humans. Both the crude emulsions and hydrocarbon-contaminated wastewater contain an enormous amount of suspended solids, oil, and grease, organic matter, highly toxic elements, high salts, and recalcitrant chemicals. The treatment of crude oil emulsion has been one of the most important challenges due to the complex nature and generation of a substantial amount of waste to meet the increasing demand for oil and its derivatives. Engineered hybrid and assembly nano- and micro-scale materials have appealed the attention of scientists and researchers because of their elegant functional structures with unique properties and promising applications in the fields of sensing, magnetic, optical, catalysis, and demulsification. Magnetic hybrid materials exhibit some interesting properties of magnets-induced separation along with recycling properties, which may favor their widespread practical uses. The modification and coating of magnetic nanoparticles with different materials having special wettability properties will not simply isolate them from external environments but also contributes to the sustainable separation of oil-water mixtures. This review elaborates on the recent research advancement on the design, fabrication, and wettability properties of hybrid magnetic materials fabricated from polymer and inorganic nanoparticles, and their potential applications in separating oil-water mixtures. After a brief introduction to the design and fabrication of nanoscale hybrid functional magnetic materials, their properties including wettability, morphology, and self-assembly are discussed. We also highlight the current research scenarios of magnetic hybrid and assembly materials along with a key role in environmental and demulsification/separation applications. Finally, the prospects of magnetic materials, ongoing challenges, and opportunities in this arena are also directed.

Contents

* Corresponding authors.
E-mail addresses: nisarali@hyit.edu.cn (N. Ali), bilaluaf@hotmail.com (M. Bilal).

https://doi.org/10.1016/j.molliq.2020.113434

1. Introduction

The key challenge of science and chemistry is the construction and design of hybrid multicomponent nanostructures with controlled homogeneity, architecture, and tunable functions of their subunits [1]. A hybrid material is defined as advanced engineering material composed of an intimate mixture of inorganic components, organic components, or both types of components. Nanoparticles of 1–100 nm and their incorporation into polymer domain can generate a wide variety of hybrid materials with proper assemblies and properties such as electrical, optical, magnetic, mechanical, and demulsification. The functional properties of these hybrid materials are because of the presence of nanoparticles and the flexibility of polymer import the processability [2–9]. Generally, organic and inorganic materials generate an integrated hybrid structure with some combined beneficial properties [10].

For innovative and tailored mechanical properties of the materials, the researchers are more interested in the soft organic component and hard inorganic components to design a proper morphology and structure [11,12]. The new nanoscale hybrids materials not only exhibit the actual properties of inorganic and organic components, but most probably to furnish fascinating characters because of the individual components combined effect of individual components, such as electrical, magnetic, and optical, properties [13]. The interesting characteristics of nanoscale hybridization show different characteristics that are significantly better than their corresponding materials [14].

Self-assembly seems a more suitable method to fabricate well-engineered, assembly, and hybrid materials by simple building blocks [15–18]. Self-assembly is a process in which a disordered system of pre-existing components forms an organized structure or pattern because of specific, local interactions among the components themselves, without external direction. On the other hand, the key challenge for the researcher in the field of material science and chemistry is to design efficient and applicable procedures to accurately control the design of self-assembly geometry and surface morphology [19–22], especially the arrangement of individual components and their ordered and homogeneity [23–25]. Instead of hybrid and assembly nanostructures with multi-components, some researchers are more focused on polymers [2,26–29]. In multi-component hybrid nanocomposite, each individual moiety possesses the value of every single portion and interesting properties derived from the collective components [30–32]. Hybrid nanostructures with different morphologies and precisely controlled geometries have attracted an intense interest [33–40].

Mostly, the laboratory level experimental work has been done in the engineering of nanoarchitecture multicomponent assembly and hybrid materials. Applications of stimuli-responsive hybrid nanocomposites i.e., temperature, light, pH, and magnetic field [41–47], oil-water separation [3–6], catalysis [48,49], gene-drug delivery [50–52], cancer diagnoses, and therapy [44–45] (Fig. 1). However, there is some reported stimuli-responsive polymer with excellent catalytic properties [53–58]. Some literature specially focused on stimuli-responsive nanocomposites containing self-assembly [59].

In the fast few years, the material with advanced interfacial/super wetting properties opened new research areas for scientists [60–62]. All amphiphilic materials (contain both hydrophobic and hydrophilic functional groups) with super wetting surfaces have gained attraction in anti-icing, self-cleaning, water collection, printing, and oil/water separation applications [63,64]. Materials with high wettability properties are always oriented for the separation of crude oil emulsions and are broadly divided into two groups, i.e. super hydrophilic/superoleophobic for the separation of water from oil and superhydrophobic/superoleophilic "separation of oil from water". Wettability is the degree at which a solid surface wetted by a liquid. Due to the high demulsification efficiency and good reusability, the separation regulated through wettability displays more advantages over conventional methods used for separation, which may have a promising perspective in the field of oil wastewater treatment including demulsification of oil/water emulsion [65–69]. Especially, the smart materials with amphiphilic properties and switchable wettability can be used for both "water removing" and "oil removing" applications.

The first-ever hybrid material for oil-water separation was reported in 2004 with smart thinking based on the gravity-driven separation of oil and water [70]. Jiang et al. inspired many researchers to develop novel magnetic Janus, raspberry, and core-shell nanoscale hybrid materials with promising demulsification applications for thick crude oil and water emulsions [3–6]. With the rapid improvement in materials inspired from fish scales of underwater superoleophobic properties (a three-phase system), i.e. oil/water/solid [71], Jiang and Feng designed and fabricated water removing filter from polyacrylamide hydrogel coated mesh, which was cited for about 606 times in the past few years [72]. As compared to the materials used for oil separation from oil and water emulsions, the water separation material acquired advantage representing the accumulation of oil on a surface of the water and hence improved the reusability.

The preparation of specific surface morphology, composition, and properties of nanoscale hybrids furnish them with some tunable and melodious properties for variable demulsification and environmental applications. During the synthesis process, when polymers part is

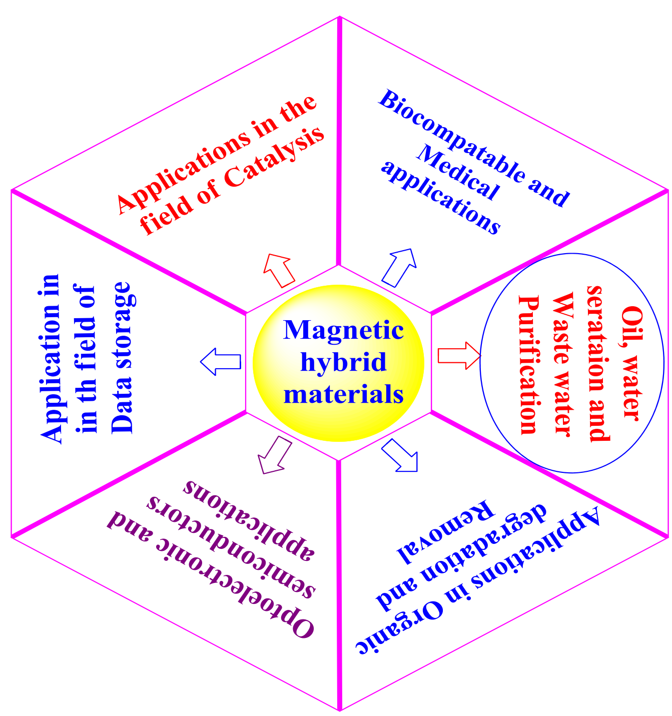


Fig. 1. Applications of magnetic composite materials.

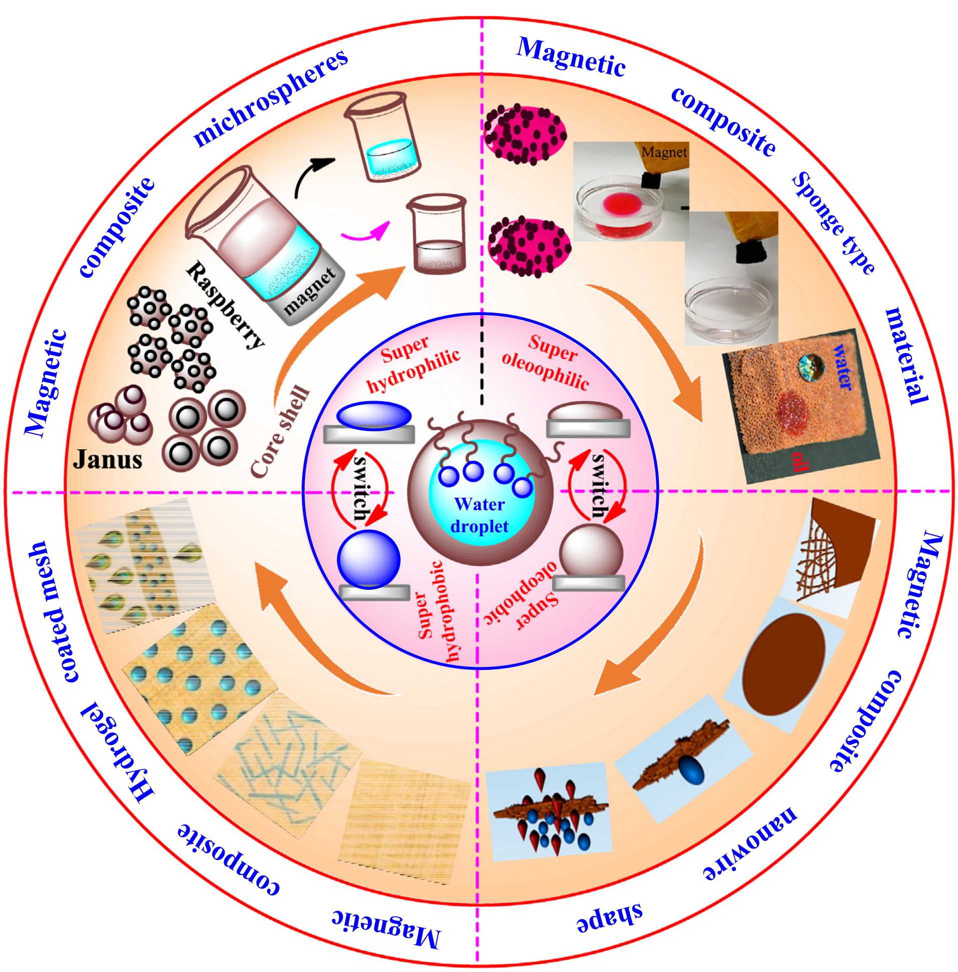
introduced, and the development of self-assembly to fabricate nanoscale hybrid and assembly materials using "grafting from", and "grafting onto" methods. Furthermore, the monohybrid and assembly materials with a proper structure such as Janus, raspberry, and core-shell are enlightening the combined properties and prospective applications [73].

This review presents the current progress in unique kinds of polymer, and metal oxide-based (Fe_3O_4) hybrid materials for diverse oil-water separation and environmental applications (Scheme 1). In the first stage, we highlighted the emulsion system, the wettability concept of the hybrid magnetic materials, and fabrication techniques for magnetic hybrid materials. The synthetic routes are briefly discussed to provide guidance and information for the synthesis and design of nanoscale hybrid assembly materials. Finally, the demulsification and environmental application of the prepared nanoscale hybrid materials are focused on appropriate mechanisms and essential principles. At the end of the review, the discussion is also made on further challenges and the outlook of organic/inorganic nanoscale hybrid materials and applications.

2. Emulsions system and physicochemical aspects

An emulsion is the mixture of two liquids, one of which is dispersed in another. For instance, if the water is dispersed in oil, the resulting emulsion is called water in oil emulsion (Fig. 2A). On the other hand, the dispersion of oil in the water produces oil in water emulsion (Fig. 2B) [74]. The dispersed phase is also referred to as the internal phase, while the other phase (continuous) is denoted as the external phase [75–79]. According to their droplet size, emulsions are categorized into three broad groups: microemulsions (10–100 nm) in the form of small aggregates, mini emulsions (20–1000 nm) in the form of relatively large droplets and macro emulsions (0.5–100 μm). The smaller the average size of the dispersed phase droplets, the more stable will be the emulsion [80]. The nature of emulsifying agents, interfacial tension, and presence of solids and bulk properties of both oil and water influence the droplet size distribution of the resultant emulsion. Generally, these emulsions apart from microemulsions are thermodynamically unstable [81–84]. However, they are kinetically stable for months or years due to the presence of surface-active compounds with their surfactant properties [85]. A stable emulsion is one that structure does not change with time, nor does it depend on how it was prepared and is characterized by small water droplets and a low conductivity [86]. The emulsion's stability can be influenced by the density of its phases, interfacial and oil phase viscosity, water droplet size, interfacial tension, surfactant concentration, film compressibility, and electrolyte concentration in the water phase [87]. In crude processes, considerable efforts have been devoted to destabilize these undesirable highly stable emulsions, mostly through a difficult, complex, and costly tasks [88,89].

The role by which emulsion type is determined is known as Bancroft's rule. This rule states that the continuous phase would be the phase that the surfactant is preferentially soluble. Therefore, a surfactant with a solubility tendency into the water phase will favor the development of oil-water emulsions. Likewise, a surfactant that is soluble into the oil phase prefers the formation of water-oil emulsions [90,91]. The water-oil emulsion type is the focus of this work, which is mostly encountered in the oil industry because of the high solubility of indigenous crude surfactant molecules in oil rather than in the water phase



Scheme 1. Illustration of magnetic hybrid material with special wettability properties.

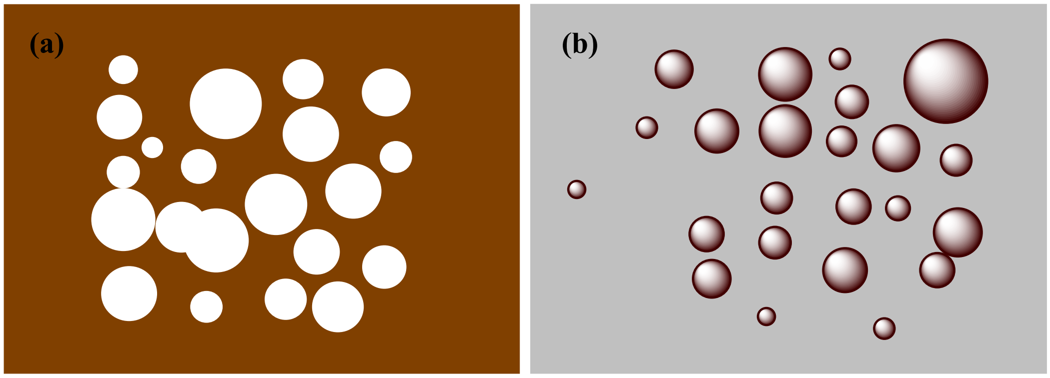


Fig. 2. Micrographs (A) water/oil emulsion and (B) oil/water emulsion.

[92–94]. These emulsions are unfortunately encountered throughout the crude oil exploitation, processing, and transportation. This widespread and occurrence of water-oil emulsions has made emulsion-based systems an important subject of investigation.

2.1. Formation of water-in-oil emulsion

The presence of emulsions is a common feature in the petroleum industry. Although the emulsions have different types, such as water in oil, oil in water, oil in water in oil, and water in oil in water, the first two are the most common [95]. There are several processes to promote emulsion formation in the petrochemical industry. The crude oil in a reservoir is naturally accompanied by gas and water formation that contains large amounts of cations such as calcium, magnesium, etc. The amount of water is constantly raised from both onshore and offshore fields where the production environment is more challenging, risky, and expensive [96]. In addition, water is also injected into depleted reservoirs for enhancing oil recovery to force the crude oil out of the reservoir. As a result, some of this water (produced water) is co-produced with oil as free water, and some of it may be in the emulsion form turbulence and pressure drop in valves at the wellhead [97]. Emulsions are also formed as the crude oil with water (formation/injected water) content is passed through choke valves and pumps due to the turbulent flow pattern developing some eddies by which a mixing effect is imposed; hence an emulsion is formed [98,99]. When the water in oil emulsion forms, the physical properties change drastically, and 60 to 80% of water leads to the establishment of stable emulsions and thus the expansion of the spillage from 2 to 5 times of the original mass. Especially, the crude oil viscosity changes from 100 mPa·s to about 100,000 mPa·s, with 500 to 1000 increasing factor. Clay is also increasing the emulsion density and kinematic viscosity and alters the liquid emulsion to the semisolid and heavy stuff, which are very difficult to remove with simple recovery instruments [100]. A schematic diagram of petroleum production and refining processes in which emulsions are encountered is given in Fig. 3.

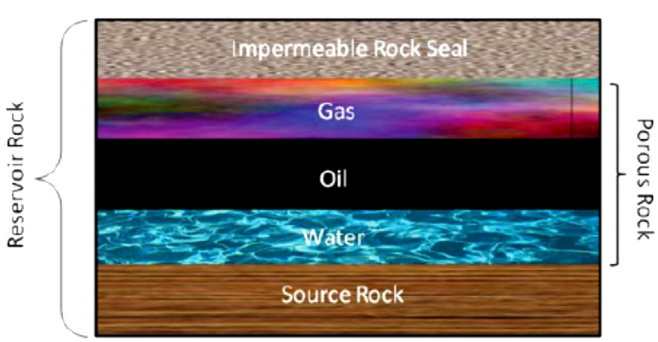


Fig. 3. Schematic diagram of petroleum production and refining processes, in which emulsions are encountered.

2.2. Stability and characterization of water-in-oil emulsion

The stability of an emulsion is mainly dependent on the stability of the interface layer between oil and water phases. Different emulsions with the same properties are stable, unstable, mesostable, and entrained water [101]. Size of emulsified phase droplets (water in case of water in oil emulsion), the viscosity of the continuous phase (oil in case of water in oil emulsion), the difference in density of the two liquids and volume percentage of water cut are also important factors that may influence the stability of an emulsion [102,103]. Asphaltene layer stabilizes the water, oil emulsion by the formation of the stable layer around water droplet, and this stability is increased by the contribution of resins, which is working as an asphaltene solvent and help in the slow migration of asphaltene. It has been found that the composition of the oil is the key factor in the formation of water in oil emulsion, including the amounts and types of saturating contents, asphaltenes, and resin [104,105]. There are some other finely divided substances such as iron, zinc and aluminum sulfates, calcium carbonate, silica, and iron sulfide, which are less soluble or dispersible in the water phase than in the oil phase, which are the responsible components for crude oil emulsions. They form a film around the surface of the dispersed water droplets. These emulsifying agents with their ability to diffuse within the interface can increase the interfacial tension between oil and water leading to broadening the interfacial layer, reduces droplet coalescence, and increases emulsion stability [106].

Higher resins to asphaltenes concentration ratio keep more of the asphaltenes aggregate dissolved in the oil phase; thereby, minimizes the number of asphaltene aggregates and reduces the stability of emulsions. In addition, asphaltenes increase the stability of water in oil emulsions through the formation of a viscous interfacial layer at the oil-water interface. This film is built up through the adsorption of asphaltenes on the finely divided solids, which are hydrophobic and naturally present in crudes such as iron and calcium carbonate. Therefore, a change in the wettability and their other characteristics occurs, allowing further adsorption of asphaltenes at the interface. However, due to the complexity, the difference in characteristics, and the chemical nature of crude oil, it is difficult to propose universal and reliable mechanisms to describe the dispersion behavior of asphaltene at the oil-water interface [107,108]. Fig. 4(a, b) shows both simple and 3D hypothetical structure of petroleum asphaltenes [109].

Studies based on the lifetime of the emulsion, visual appearance, elasticity, differences in viscosity, the stability is categorized into four classes namely, stable, unstable, mesostable emulsions, and entrained water. The last one is a black color emulsion with the water content of less than 10% entrained by viscous oil. Stable emulsions are reddish to brown in color, contain 80% water, and can exist for several weeks with higher viscosity at least three times than the original oil viscosity. This viscosity increase is attributed to the asphaltenes and resin's ability to align at the interface, creating strong viscoelastic films. In unstable emulsions, water and oil separate in a matter of a few hours with a

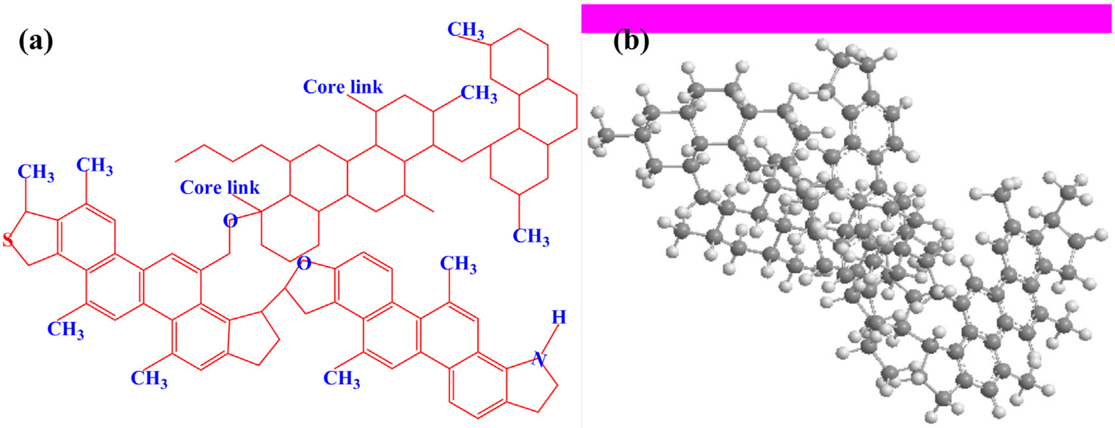


Fig. 4. (a) Proposed molecular structure asphaltenes and (b) 3D constructed using Chem draw software.

water content lower than 50%. Their final viscosity is 20 times greater than the original oil viscosity. The emulsion's color is the same as the starting oil's color, which can be black or brown. Mesostable emulsions are red, black, or brown in color. This is an unstable emulsion due to their aromatic, aliphatic, and little asphaltene content, and a tendency to destabilize easily, but their high viscosity renders them stable for a period. Upon decomposition, they produce layers of oil and stable emulsions [110,111]. In addition, due to the acidic nature of the active compounds of the oil/water interface, pH also exhibits an effect on the film and emulsion stability. Increasing the pH was found to be associated with the ionization of the polar functional groups in both asphaltene and resin molecules. Due to this ionization, high surface charge densities are developed resulting in changing (destroying), the mechanical film properties through some internal repulsive interactions, which ultimately may reduce the emulsion stability [112]. The temperature is also found to influence emulsion stability. Increasing the emulsion temperature leads to a decrease in the oil phase viscosity and an increase in the collision rate between water droplets, which ultimately reduced the system (emulsion) stability [113]. Some processes including dispersed phase drop flocculation and coalescence, however, can influence the stability of this layer. For the flocculation, low repulsion forces, and fairly high adhesion character lead drops approach each other, the film around the water droplets undergoes thinning and eventually ruptures, this latter process is referred to as coalescence [114].

3. Emulsion destabilization methods

Emulsion formation is an inevitable phenomenon in the crude oil industry due to water and oil contact during oil processing. In the previous parts of this study, it is clearly explained that surface-active compounds have an enormous problematic influence on the petroleum industry throughout production and refinery stages through emulsion stabilization. The emulsion stability is proportional to the crude oil content of these emulsifiers and their interactions. The higher content of these surface-active compounds contributes to emulsion stability [115–117]. Therefore, demulsifying these emulsions i.e. reversible flocculation followed by irreversible coalescence of the dispersed (water) phase droplets and eventually creating two distinctive layers of oil phase on top and water/aqueous phase at the bottom is important to meet pipeline and exportation specifications. However, it has been a difficult procedure in the oil industry, otherwise, severe processing problems arise such as pipes and equipment corrosion, catalyst poisoning, and difficulties in transportation [118–120].

To effectively and economically demulsify water-oil emulsions, it is important to understand their stability behavior or mechanism that requires knowledge of asphaltenes and resins properties and interactions as they have been considered as the main emulsion stabilizers. Other aforementioned stabilizers are also important due to their strong tendency to interact with asphaltenes and/or resins. Currently, there has been progressing in chemical, thermal, and electrical demulsification methods. Chemical treatment through the use of chemical demulsifiers (surface active agents) is considered the main method to separate these emulsions. The heating/microwave demulsification and electro demulsification have also been in use for this purpose. The combination of these two techniques has also been attempted to enhance demulsification efficiency. Microfiltration was employed to break down water-oil emulsions. Although all these techniques have been demonstrated to be efficient, their utilization cannot fully satisfy the prerequisites of oil-water separation. It is worth observing that there is no universal method that can be applied for all emulsions, i.e., the methods are very applicable/crude specific, with the trial and error principle has been the basis to decide the applied method for a given emulsion.

3.1. The concept of surfaces wettability

Wettability of materials initially can be explained using Young's equation in 1805 [121], and the direct route to study the surface wettability is by calculating the oil-water contact angle (OCA) and water-oil (WCA) of a liquid droplet attached directly by the base in the air [122,123].

The detailed information of different kinds of special wettability surfaces and their contact angles is given in Fig. 5 [124–129]. The contact angle is the angle at which the liquid-vapor interface contacts the liquid-solid interface. Generally, it is used to estimate the surface wettability against liquids. The contact angle explains the strength of contact between solids, liquids, and air. Many experimental studies were conducted on wettability and the development of tunable hydrophobic and hydrophilic materials [130,131], especially for the separation of oil-water mixtures [132,133] and the prevention of biofouling [134]. In this part of the review, we shortly discuss the existing model of wettability as solid/liquid and air followed by solid/liquid and liquid systems.

The contact between solid and liquid (CSL) in the air is explained by Eq. (1) [135].

$$C_{SL} = \delta_L + \delta_S - \gamma_{SL} \quad (1)$$

σ_L is for liquid's surface tension i.e. aqueous (aq) phase or oil (o) phase, σ_S indicates the free energy of solid's surfaces, while γ_{SL} is the interfacial energy of solid-liquid interface.

Young measured the solid-liquid and air contact angle as mentioned in Young's equation, expressed in Eq. (2).

Wettability	Water contact angle °	Wettability	Oil contact angle °
Hydrophilic	< 90	Oleophilic	< 90
Super ydrophilic	~ 0	Super oleophilic	~ 0
Hydrophobic	> 90	Oleophobic	> 90
Super hydrophobic	> 150	Super oleophobic	> 150

Fig. 5. Explanation of wettability in terms of water and oil contact angles.

$$\gamma_{SL} - \gamma_{SV} = \gamma_{LV} \cos\theta_C = 0 \quad (2)$$

γ_{SL} explain the solid/liquid interfacial energy, γ_{SV} solid/vapor interfacial energy, and γ_{LV} is for liquid-vapor interfacial energy. Fig. 6(a, b) show the schematics explanation of water/oil droplet on solid surfaces into the air.

In the case of the rough surface when the contact angle is calculated the Wenzel or Cassie-Baxter models can be used [136]. On a rough surface, the relation between Young contact angle and contact angle of the liquid has been calculated according to the surface state of wettability, as explained by Wenzel [137] and Cassie-Baxter [138], where surface roughness plays a very important role to calculate the contact angle in both Wenzel and Cassie cases. Wenzel state, in a homogeneous wetting state, when the liquids contact on to the complete rough surface (Fig. 8) and explained in Eq. (3).

$$\cos\theta_C = r \cos\theta_Y \quad (3)$$

where r is the ration of the roughness, θ_Y is Young contact angle of liquid placed on a smooth surface when, and θ_C is the visible contact angle. Fig. 7(a, b, c and d) explain the wetting behavior of rough solid surface both in air and underwater.

Contrarily when the air trapped inside the rough surface in liquid Cassie-Baxter explains the condition in a heterogeneous wetting system, explained in Eq. (4).

$$\cos\theta_C = r_f f \cos\theta_Y + f - 1 \quad (4)$$

f is the solid surface fraction under the droplet fraction, r_f is for the wetted area roughness; Young's contact angle of the sold surface at equilibrium is θ_Y, and θ_C shows the apparent contact angle.

4. Fabrication of magnetic hybrid nanomaterials

In recent years, various approaches have been proposed to fabricate hybrid materials [139–144]. Reactive sites on polymer surface used for the establishment of the polymer layer by the monomer polymerization in "grafting from" method and the polymer chemical reaction through covalent bonding with the end functional groups "grafting to" method. The most common fabrication techniques of hybrid materials are γ-ray irradiation, plasma modification, and UV photo-induced graft polymerization. The most applicable method is grafting polymerization for the modification of polymer surface functional groups with more effective groups [145–148]. Firstly, the polymer should be designed, prepared, and characterized for some practical applications. In order to check the oil, water separation applications, the surface of the polymer can be modified with hydrophilic and hydrophobic groups. The "grafting polymerization" method has been applied to attach polymers to nonporous and flat surfaces, but with very limited applications [149–151] (Fig. 8).

For applications perspective, the core-shell microspheres have major advantages over simple microspheres leading to the enhancement of properties such as (i) less cytotoxicity, (ii) increase indispensability, (iii) increased thermal and chemical stability and so on [152,153]. Various well developed polymerization methods such as atomic transfer radical, soap-free emulsion, inverse, and mini emulsion are, in practice to effectively fabricate magnetic composite materials for numerous applications [154–156]. Isotropic microspheres having self-assembly properties are well known to the researchers but do not show many ways to achieve proper structures [157].

Recently, microfluidics has been used to develop microspheres and some interesting results have been achieved [158]. In the case of crystals, the shape of nanoparticles through artistic management is more

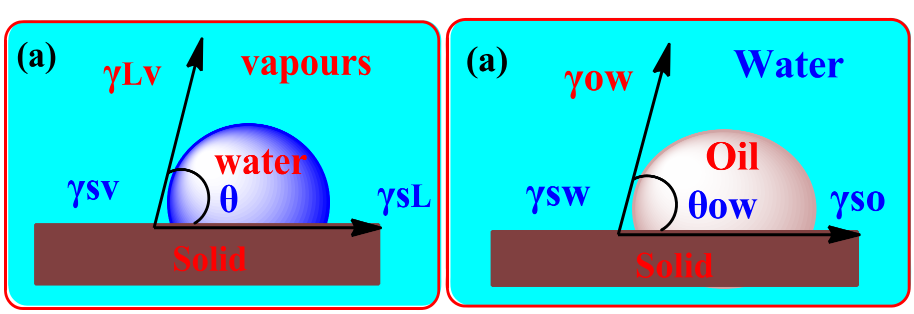


Fig. 6. Young wetting states of liquid droplet on solid smooth surfaces in the air: (a) and underwater (b).

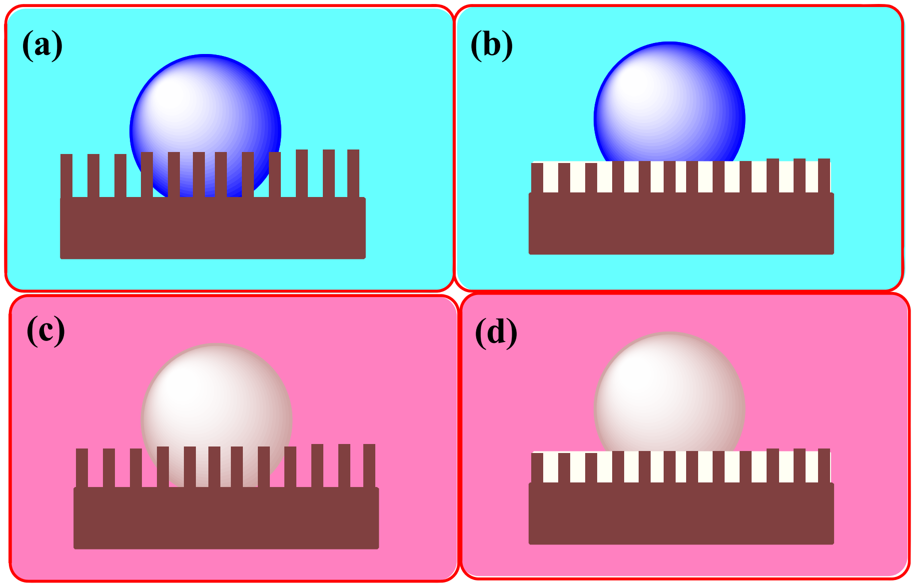


Fig. 7. Wetting states of oil droplet on various underwater solid surfaces: in the air Wenzel state (a) and Cassie state (b) and underwater and Wenzel state (c) and Cassie states (d).

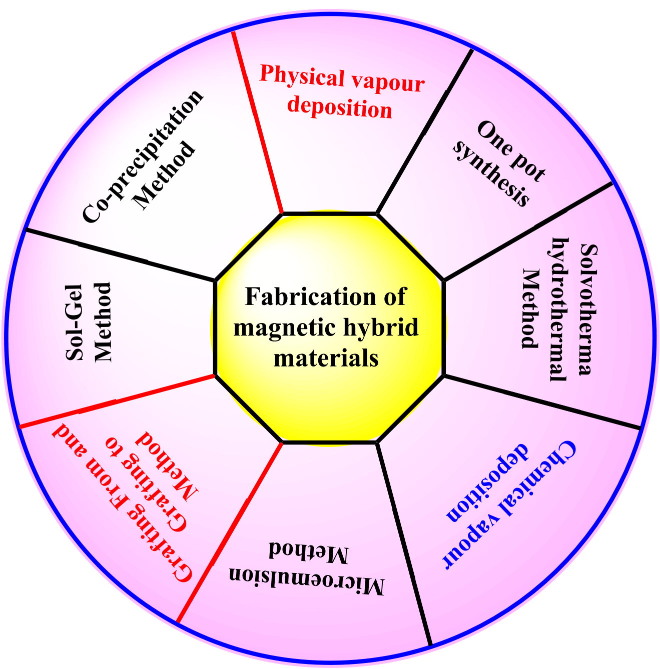


Fig. 8. Fabrication techniques of magnetic composite materials.

challenging and has been achieved successfully [159]. Some other prepared hybrid materials in anisotropic shape or taking in an anisotropic distribution of different functional groups, in which the material particles can be split into two sections and each component formed from dissimilar materials or having different functional groups [160]. They mimic the behavior of such anisotropic or Janus type materials i.e. surfactants, which showed different functionalities like hydrophilic, hydrophobic with a remarkable self-assembly behavior. Therefore, an enormous interest has been noted in Janus type hybrid materials, which is confirmed by the publication of research articles on this topic [161,162].

Janus microspheres can be prepared by three distinct methods, one of which is the self-assembly of components i.e. mixture ligands and block copolymers (polymeric micelles) [163–167]. The second method to prepare Janus type hybrid material is called masking step in which the functionalization or polymerization chemical reaction takes place on one portion of the nanoparticle because the other side of the nanoparticles is made to be inaccessible to some reagents [168–171]. The third method is either simple phase separation of different polymers using the phase segregation of the inorganic part outside or interior of the polymer [172–177], or phase separation of two similar inorganic components, especially to make nanocrystalline dimmers [178–182]. Additionally, experimental work shows, close to the very exceptional computational design of Janus type materials published, which support the existing results [183–187]. Moreover, there is much-focused research work on the self-assembly of Janus type hybrid materials and their surface activity [188–190]. Fig. 9 summarize different shapes and morphologies of magnetic composite materials.

Chemistry of hybrid materials can be improved, which let the properties of different to be lent to the nanoscale material [191]. The past theoretical and experimental research elucidates the microsphere's adsorption liquid/liquid interfaces and the stability of emulsion [192,193]. In addition, the stimuli-responsive polymer is one of the promising set of materials in this context [194]. The combination of stimuli-responsive polymers with some suitable inorganic components to successfully produce a composite fabric with some promising properties such as their application to employ them in the oil, water interface [195–200]. To fabricate multilayered hybrid material self-assembly of the inorganic component in the oil-water interface can be used [201].

The most essential part of hybrid material is its organic part, which imports a diverse range of fabrication and construction design to the assembly material. It is very much important that the surface of inorganic nanoparticle should be functioned with an organic component to balance or regulate the interaction of nanoparticles and other organisms [202–204]. The surface of the nanoparticle should be paved with organic component or ligand with low toxicity and varied range of applications [205]. The organic component possesses stability, high dispersibility, flexibility, and creative functionality. For example, the modification and functionalization of the surface of nanoparticles with suitable organic components can import promising properties and site-specificity. This mostly depends on the organic components attached to the nanoparticle surface and also the properties and nature of the nanoparticles in the end [206]. An

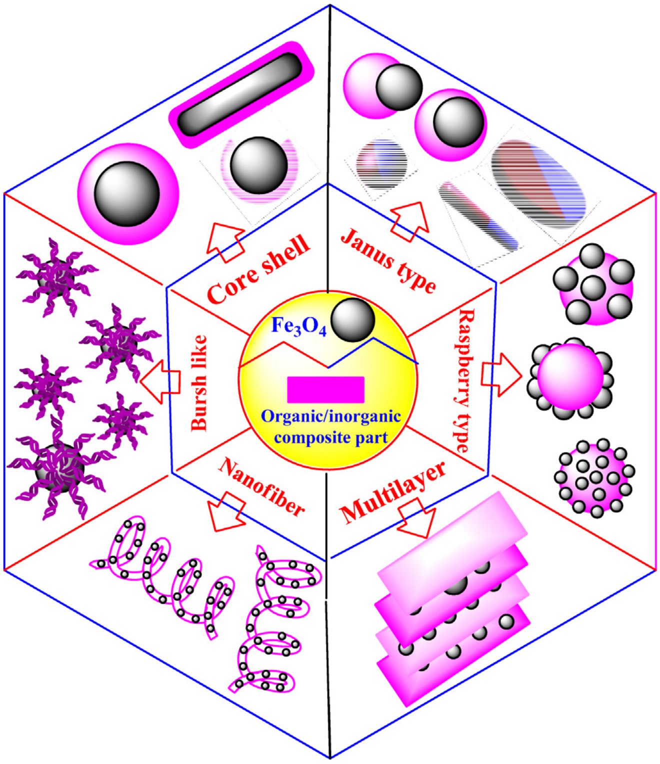


Fig. 9. Different shapes of magnetic composite microspheres.

example, the surface of gold-nanoparticles may be functionalized with the ligands of the thiol group and the silica surface is better to functionalized with silane component. The double hydroxide layer possesses some unique features while making the exchange of anions within the inner layers and utilized for the organic anions carriage.

5. Magnetic hybrid materials at the oil-water interface

Bearing in mind the chemical, thermal, electrical and filtration processes for demulsification of water-oil emulsions with their limitations, herein, we elucidate a new family of amphiphilic, superoleophilic/superhydrophobic and hydrophobic/superoleophilic hybrid and assembly materials with different shape, morphology, and architecture as emulsion destabilizer. The primary advantage of this hybrid material is to separate oil, water emulsion in a very short time, low temperature, reduced sludge formation and oil loss. Many of these materials may be magnetic in nature with a strong magnetic domain and can be reused several times, also do not contaminate the separated emulsion. The intention is to review general hybrid and assembly materials, separation processes from the varieties of other processes available, historical aspects and mechanistic points of view. The effect of different operating conditions for the performance of hybrid and assembly materials is also summarized.

Magnetic polymer microspheres constitute an advanced macromolecule material, composed of a polymer and an inorganic magnetic material exhibiting the dual characteristic features. The magnetic material endures the microspheres with superparamagnetic properties enabling the particles to be conveniently separated from a solution under the external magnetic field and can be reused without any high-energy operation and cost such as filtration and centrifugation [207]. Magnetic hybrid materials, particularly the encapsulated magnetite (Fe_3O_4), exhibits a broad range of applications including target drug delivery, hyperthermia therapy, purification/separation, catalysis and so on [208–210]. The transition of the Fe_3O_4 functionalities by encapsulating Fe_3O_4 through polymers to make a versatile core-shell magnetic hybrid material [211]. Xu et al. used seed emulsion polymerization having seeds of magnetic nanoparticles to prepare magnetic polymer hybrid material in control shape, size and desirable interfacial functionalities [212].

Magnetic materials exhibit special magnetic properties that can be recovered for reuse from the multiphase complex systems. In the past few years, these materials have attracted a significant research interest [213–215]. Magnetic hybrid materials are carriers for their diverse applications because of strong magnetic responses and easy separation of a complex multiphase system by an external magnetic field. Magnetic nanomaterials have been extensively applied in a variety of fields, such as separation and purification [216], catalysis [217]. Among these, Fe_3O_4 is considered an ideal candidate because of its good compatibility and low cytotoxicity [218]. Table 1 explains the summary of magnetic hybrid material with application in the separation of oil and water emulsion. The grafting of magnetic nanoparticles with brushes charged polymer in order to study the advantages of combine charged polymer brushes on the magnetic nanoparticles hydration effect, having a large surface area, maybe promising material for oil-water separation [245–247]. The grafting poly(3-sulfopropyl methacrylate potassium salt) (PSPMA) brushes-grafted Fe_3O_4@SiO_2 magnetic composite nanoparticles having negatively charged and strong hydration capacity in aqueous solution because of the presence of PSPMA brushes [248] that can pick up the present water droplets in an oil-water emulsion. Silica coating can be used to cover the Fe_3O_4 nanoparticle cores from further aggregation and damage and produces proper supporting media to combine active functional groups like Si-OH groups [250]. When the prepared magnetic composite nanoparticles were applied for separation of an oil-water mixture, the dispersed water droplets gathered to form a big hydrate, which was easily separated by an external magnetic field [220] (Fig. 10).

More recently, the fabrication of polyurethane with iron oxide and polystyrene in a two-step method generated PU@Fe_3O_4@PS magnetic sponge with superhydrophobic properties [222]. Photopolymerization and grafting with ultrasonic dip coating was used to effectively attach the polystyrene and iron oxide Fe_3O_4 nanoparticles on the surface of polyurethane sponge and thus prepared a well-engineered, hydrophobic nano-sized surface as explained in Fig. 11(a). As the photopolymerization is one of the facile methods for the surface modification of polymers [251,252]. The prepared superhydrophobic PU@Fe_3O_4@PS sponge exhibits the excellent capacity of adsorption and reusability. Therefore, PU@Fe_3O_4@PS sponge was applied to selective adsorption of different organic solvents and oil factions from water. It was concluded that PU@Fe_3O_4@PS sponge shows the efficient separation of oil, water mixtures if used in combination (Fig. 11(b, c, and d). Furthermore, the strong magnetic property made the superhydrophobic PU@Fe_3O_4@PS sponge more convenient for multiple time reusability after magnetic separation.

Fe_3O_4/SiO_2 magnetic hybrid core-shell porous microspheres were prepared through a very simple template fabrication approach, while the superhydrophobicity of the prepared Fe_3O_4/SiO_2 was improved by using vinyl tri ethoxy silane (Fig. 12). The modified Fe_3O_4/SiO_2 magnetic hybrid core-shell microspheres with porous characters showed an excellent absorption capacity of floating oil content from the surface of the water. They exhibited a slight decrease in the absorption and contact angle after 20 times successive reuse cycles [223]. Ali et al. [6] designed novel amphiphilic hybrid polymer magnetic microspheres with a core-shell structure (Fig. 13). The copolymerization of monomers MMA, GMA, and DVB on the Fe_3O_4 nanoparticles surface followed by surface modification with epoxy groups on the shell of the prepared polymer by an amino group created intelligent hybrid polymeric hybrid core-shell material with magnetic core, good interfacial properties, and separation

Table 1
Nano-scale magnetic hybrid materials at oil-water interface.

Type of magnetic material	Wettability	Synthetic route	Emulsion type	Separation (%)	References
Polyvinylpyrrolidone (PVP)-coated iron oxide		Solvothermal/coating	Storage oil/water	100	[219]
Poly(3-sulfopropyl methacrylate potassium salt) (PSPMA) brushes-grafted $Fe_3O_4@SiO_2$	Hydrophilic	Solvothermal/hydration effect	n-Hexane/water		[220]
Carbon nanotube-poly(vinyl alcohol) (CNT-PVA)	Underwater superoleophobic		Crude oil/water	70–80	[221]
PU@Fe_3O_4@PS sponge	Upper hydrophobic	Self-initiated photografting and photopolymerization (SIPGP)	Diesel/water	99.4	[222]
Vinyltriethoxysilane/Fe_3O_4/SiO_2	Hydrophobic/Oleophilic	Fabrication	Diesel/water		[223]
Fe_3O_4/graphene oxide/MgAl-layer double hydroxide		Layer by layer fabrication	Gasoline/water Diesel/water Crude oil/water	98.5 99.0 99.2 99.8	[224]
$Fe_3O_4@SiO_2$—NH_2/cyclodextrins (CDs)	Hydrophilic exterior/hydrophobic interior	Fabrication	Crude oil/water	100	[225]
Poly(styrene-divinylbenzene) (Poly (St-DVB)) Fe_3O_4	Hydrophobic	Polymerization/fabrication	Gasoline/water Diesel/water	92	[226]
Fe_3O_4/PS	Hydrophobic/superoleophilic	Solvothermal/precipitation polymerization	Diesel/water		[227]
Polystyrene/Fe_3O_4/graphene aerogel	Hydrophobic	Solvothermal/dispersion polymerization/	Crude oil/water	99.7	[228]
Polyurethane@$Fe_3O_4@SiO_2$@Fluoropolymer sponges	Superhydrophobic	Coprecipitation/chemical vapor deposition (CVD)	Petrol/water		[229]
Ethyl cellulose (EC)/carboxymethyl cellulose (CMC)/magnetite (Fe_3O_4)	Hydrophobic	Solvothermal/fabrication	Toluene/water	96.76	[230]
Polydimethylsiloxane (PDMS)/$ZnFe_2O_4$		Solvothermal/coating	n-Hexane/water	98	[231]
Poly{3-[dimethyl(2-methacryloyl oxyethyl) amino]propanesulfonate} (PDMAPS)/Fe_3O_4	Superhydrophilic	Solvothermal/RAFT polymerization	Crude oil/water		[232]
Polyvinyl pyrrolidone coated magnetite nanoparticles		Hydrothermal/coating	Hexadecane/water Dodecane/water	100	[233]
Ethyl cellulose (EC)/Fe_3O_4	Amphiphilic	Grafting	Water/diluted bitumen	90	[234]
Poly(vinylidene fluoride-hexa fluoro propylene) (PVDF-HFP)/Fe_3O_4	Hydrophobic	Solvothermal/single-step dipping fabrication method	Petroleum ether/water	92.32	[235]
Triethoxy (1H, 1H, 2H, 2H heptadeca fluorodecyl) silane (TEHFDS)/Fe_3O_4/melamine sponge	Superhydrophobic	One-pot solvothermal	Chloroform/water	85.3	[236]
Cellulose sponge (CE)/hexa decyl trimethoxysilane/Fe_3O_4	Superhydrophobic	Solvothermal/sol—gel method and freeze drying	n-Hexane/water Toluene/water Cyclohexane/water, Paraffin oil/water	95 97 98 96	[239]
Steel mesh/ferric stearate ($Fe[CH_3(CH_2)16COO]_2$)	Superhydrophobic/superoleophilic	Fabrication	Crude oil/water		[240]
Melamine-formaldehyde sponges/Fe_3O_4	Hydrophobic/oleophilic	Fabrication	Tetrachloromethane/water n-Hexane/water Gasoline/water		[241]
(3-glycidoxypropyl) tri methoxy silane (GPTMS) Epoxy group functionalized $Fe_3O_4@SiO_2$		Solvothermal/fabrication	Crude oil/water	70.4	[242]
Quartz fiber (QF)/polydimethyl siloxane (PDMS)/Fe_3O_4	Hydrophobic	Fabrication	n-Hexane/water Toluene/water Gasoline/water	99	[243]
Fe_2O_3/Carbon, Cobalt/C, and Ni/C foams, polyurethane sponge/poly (acrylic acid)	Hydrophobic	Polymerization	Crude oil/water n-Hexane/water Diesel/water Octane/water Gasoline/water	95 86 80 84 90	[244]
Poly(methylmethacrylate-acrylic acid –divinyl benzene)/iron oxideP(MMA-AA-DVB)/Fe_3O_4	Amphiphilic	Solvothermal/emulsion polymerization	Crude oil/water	99	[3–5]
Iron oxide @poly (methyl methacrylate –acrylicacid-divinylebenzene) (Fe_3O_4@P(MMA-AA-DVB)	Amphiphilic	Solvothermal/distillation precipitation polymerization	Crude oil/water	96	[6]

capacities. The designed amino-modified Fe_3O_4@P(GMA-MMA-DVB) magnetic composite microspheres have the ability to properly migrate to the oil-water interface and disturb the structure of natural emulsifying surfactants (asphaltenes) and thus separate water from crude oil [6]. In another study, the same group investigated the demulsification properties of magnetic composite microspheres to improve the demulsifying efficiency with respect to time, temperature and concentration of demulsifiers and prepared a new core-shell magnetic composite microspheres, iron oxide@poly(methyl methacrylate-acrylic acid-divinylbenzene) (Fe_3O_4@P(MMA-AA-DVB) magnetic composite microspheres. The hydrophilic amino group of amino-modified P(GMA-MMA-DVB) was replaced with the carboxylic group and prepared Fe_3O_4@P(MMA-AA-DVB) magnetic hybrid materials with proper core-shell morphology (Fig. 14). In the prepared Fe_3O_4@P(MMA-AA-DVB) microsphere, there is a hydrophobic alkyl and hydrophilic carboxylic group, and the P(MMA-AA-DVB) *co*-polymer shows good amphiphilic and interfacial properties. The as-prepared magnetic hybrid microspheres leading to

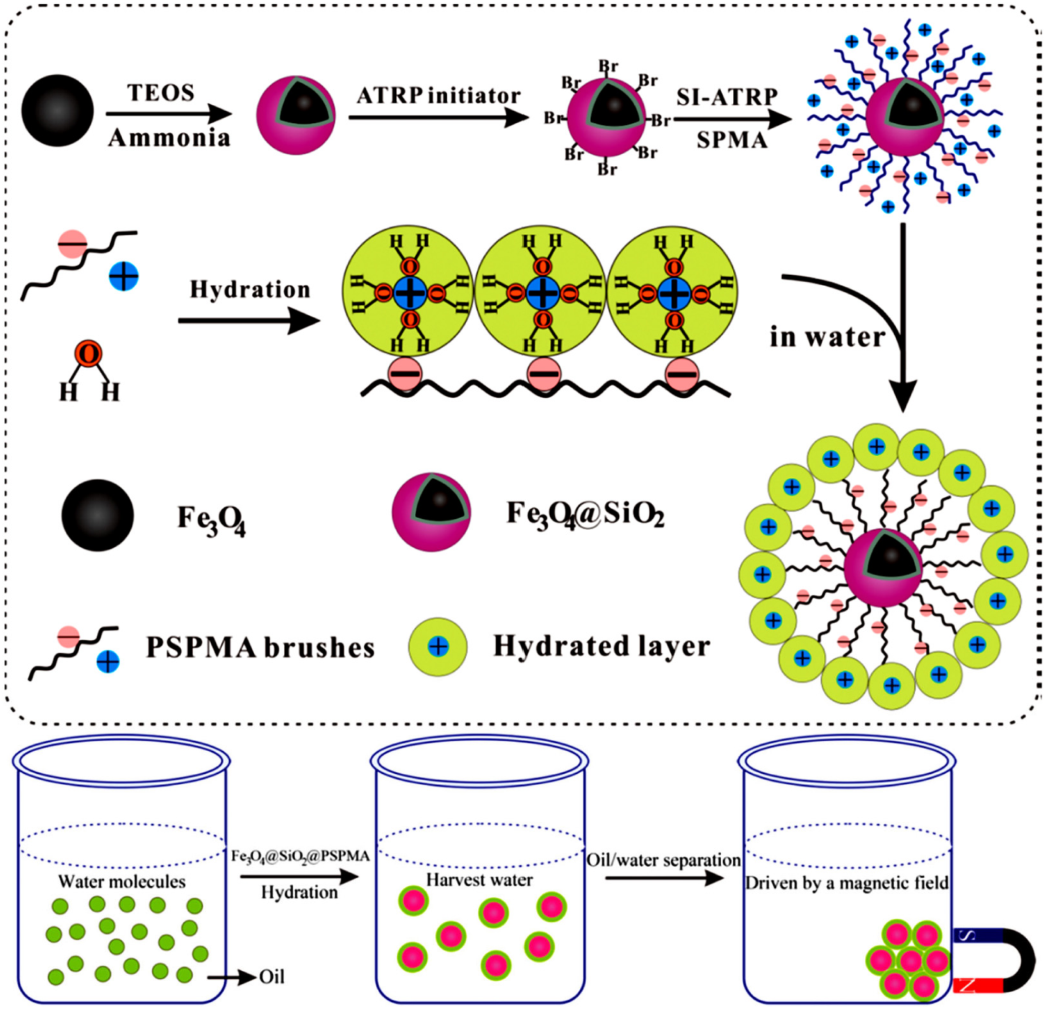


Fig. 10. Possible explanation of the e charged polymer brushes-grafted magnetic composite core-shell nanoparticles (Fe_3O_4@SiO_2@PSPMA), PSPMA brushes hydration mechanism, and oil/water separation.
Reprinted from Ref. [221] with permission from the American Chemical Society. Copyright (2014) American Chemical Society.

quick separation under the magnetic response. Therefore, Fe_3O_4@P(MMA-AA-DVB) magnetic hybrid material can give a rapid phase separation for demulsification by an external magnetic field because of enhanced coalescence and controlled movement of stable water droplets [5]. Ali et al. [3] further improved the demulsification efficiency of Fe_3O_4@P(MMA-AA-DVB) magnetic hybrid material by the modification of the structure from core-shell to Janus type. They designed Janus type P(MMA-AA-DVB)/Fe_3O_4 magnetic hybrid material with enhanced surface properties, tunable structural anisotropy, the higher domain of magnetite, and high amphiphilic and wettability properties. In an oil-water emulsion, Janus magnetic hybrid material exhibits interfacial properties, enhanced the coalescence of water droplets and rapid separation of the water phase from oil in emulsion by an external magnetic field (Fig. 15).

Further, the P(MMA-AA-DVB)/Fe_3O_4 magnetic hybrid Janus material revealed excellent demulsification of crude oil-water emulsion with inspiration that the morphology of magnetic particles may be an important factor affecting its demulsification properties. Therefore, a completely new and more effective demulsifier comparing with P(MMA-AA-DVB)/Fe_3O_4 magnetic composite microspheres with the raspberry-like structure were prepared (Fig. 16) [4], which can destabilize oil and water emulsion quickly, at low temperature, and can be reused many times.

Zhang et al. fabricated magnetically recoverable interfacial hybrid material modified with cyclodextrin (MCDs). Though MCDs modified nanoparticles demonstrate more hydrophilic properties, the intelligent M-CDs can be easily switched from hydrophilic to hydrophobic characters spontaneously because of the inclusion complexes (ICs) formation between cyclodextrin/oil at the oil-water interface. Physicochemical characterization and the amphiphilic properties of modified cyclodextrin revealed that the material can adsorb at the oil, water interface and can be observed on the surface of the droplet like a Pickering emulsifier. With the application of external hand-magnet, the modified cyclodextrin can be recovered from the surface of the droplet and leads to the effective separation of oil-water emulsion [229]. The encapsulation of iron oxide with hydrophilic carboxymethyl cellulose (CMC) through the process of adsorption in aqueous solution by hydrogen bonding and electrostatic force of attraction produced interfacially active and dispersed M-CMC nanoparticles with Janus like structure (Fig. 17) [230]. The prepared material displayed exceptional interfacial properties, which were investigated by interfacial pressure-area isotherms (π-A), and coalescence time (using induction time). Magnetic composite Janus nanoparticles were successfully applied to the oil, water emulsion leading to effective phase separation of the emulsions and the oil-contaminated wastewaters [253].

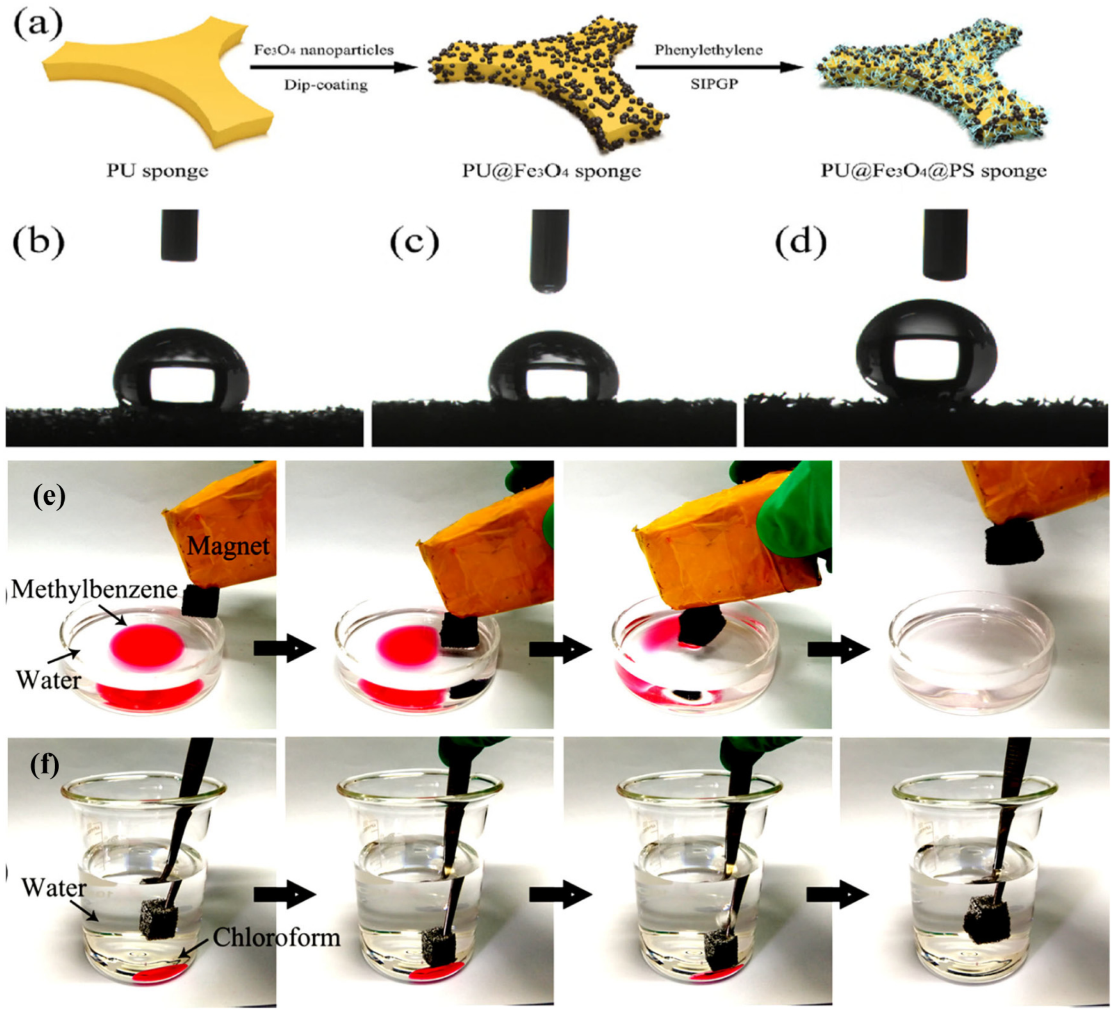


Fig. 11. (a) Explanation for preparation of PU@Fe_3O_4@PS sponge; The WCA of (b) PU sponge, (c) PU@Fe_3O_4 sponge and (d) PU@Fe_3O_4@PS sponge and adsorption processes of (e) methylbenzene in water surface and (f) chloroform underwater.

6. Up-gradation to a commercial level and challenges

Though there are many advantages of magnetic hybrid materials with distinct wettability properties having applications for the sustainable separation of oil, water mixtures, the approaches of their fabrication and applications are still experienced at laboratory scale and required to upgrade at the pilot and commercial level. Their large scale processing faces several challenges such as (1) on-site bulk or large volume processing (2) high accuracy with the standard operation, effective and suitable working conditions, (3) health, safety and environmental perspective for the large and commercial level production need to be addressed in a more effective manner. The progression in the modern key technologies suggests the up-gradation strategies to sustain the large scale processing and production on-site. Variation and accuracy in the production process are also one of the major concerns to supply magnetic hybrid material having special and switchable wettability properties according to the market needs. Consequently, more state of the art and sophisticated strategies undoubtedly will improve the existing fabrication procedures at commercial level.

7. Conclusions and future perspectives

In this review, we summarized the recent advancements in the fabrication of magnetic hybrid material with smart surfaces, tunable wetting properties and their potential applications in a controlled separation of oil-water mixtures. The separation behavior, vital theories and principles for the design and preparation of smart materials for effective separation are discussed in detail. This effort may provide a useful guide to research candidates in the future in this field of science and engineering. Additionally, the external stimuli-responsive magnetic materials have also been comprehensively explored to govern the process of separation. Other separations based on smart magnetic hybrid materials and polymers were also addressed because these materials have a noteworthy contribution to the oil-water separation field. For example, electric and light-responsive polymers may be helpful for the transfer of wettability and quick separation. Magnetically responsive smart materials definitely facilitate the process of separation and the collection of absorbents using a simple magnetic process. Generally, the development of emulsion breaking and separating the use of hybrid magnetic polymeric materials separation materials provide excellent results, which import potential applications. Most of the smart magnetic materials exhibit the separation efficiency of extremely high levels reaching beyond 99.99%. In addition, most of the reusable materials showed excellent separation performance even after the use of many times. After studying and completion of this review, it is clear that some smart magnetic materials develop extra high separating materials with

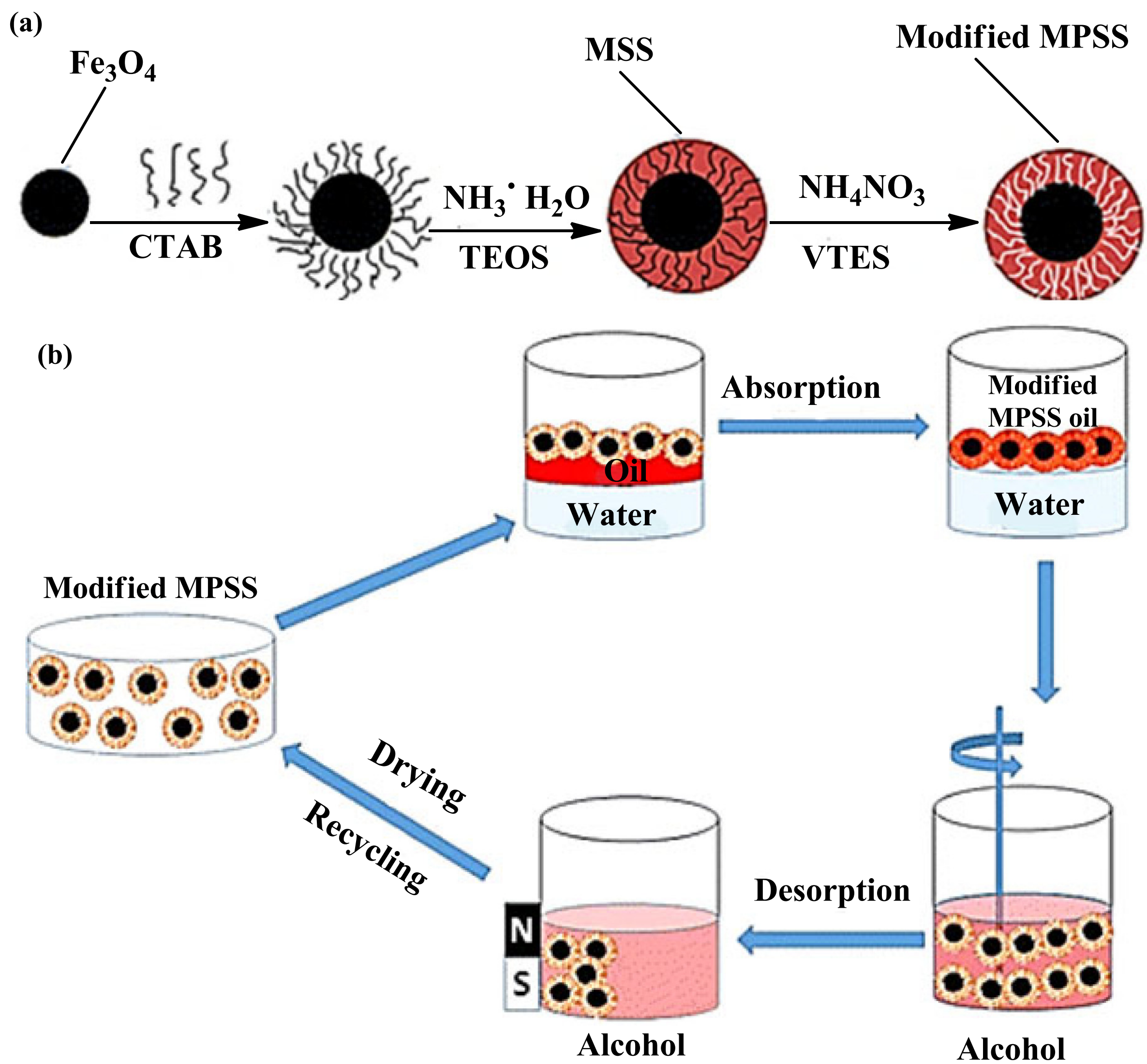


Fig. 12. (a) shows the fabrication mechanism of the Fe_3O_4/SiO_2 magnetic composite core-shell microspheres and (b) explain the water separation and reusability of the modified MPSS. Reprinted from Ref. [224] with permission from the American Chemical Society. Copyright (2015) American Chemical Society.

responsive surfaces, which open new directions in the field of polymers and environmental science and engineering. Although a promising advancement has been achieved in the design and preparation of hybrid magnetic materials for effective oil-water separation, there are some problems to be properly handled related to the theories of surface super wetting and applications.

1) Surface wettability is the first scientific and complex problem. Recently, most of the synthetic procedures (e.g., in situ polymerization) are laboratory-based and are not applicable for the production at a high level. Indeed, some new principles were used for the fabrication of extremely promising magnetic materials for the separation of oil and water emulsions. Also, the problem of deterioration of responsiveness and reduction in separation ability needs to be properly addressed.
2) For materials with pH-responsive ability, the pre-wetting treatment is required for the separation devices with specific pH aqueous solution, but it is important that the pH of the surrounding medium would change during the separation. Although this problem may be more dangerous if the device is used for multiple attempts of separation. At this stage, other separation assisting methods like physical stimuli (e.g. light, temperature, electric field, etc.) may add more advantages. Therefore, the development and synthesis of these hybrid and smart materials are of high value and more encouraging for future research. Furthermore, the water contaminated with oil or oil and water emulsion also contains heavy metal ions and microorganisms.
3) Though most of the materials are excellent in oil-water separation but do not account for the problem of heavy metal ions. Therefore, some stimuli-responsive and multifunctional material having the ability to separate both oil and water mixtures and remove heavy metal ions from the contaminated media with antimicrobial properties are the need of the day. For example, the incorporation of some functional groups, which have the ability of complexation with a metal ion (e.g. Carboxyl group) into the polymer for the removal of heavy metal ions. Photocatalytic degradation is mostly possible with the irradiation of UV light toward microorganisms and organic compounds. Therefore, the addition of UV light-sensitive nanoparticles like TiO_2 and ZnO into the polymer to prepare materials may show broad applications both antifouling in the switching wettability.

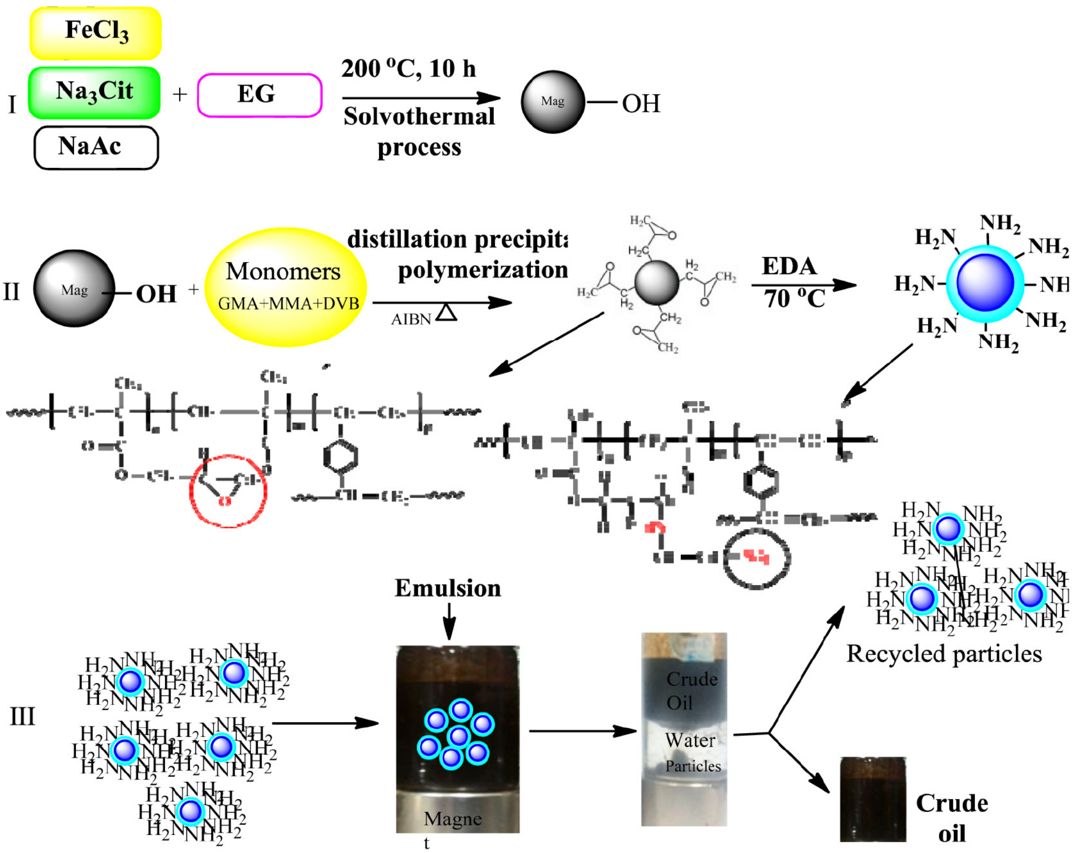


Fig. 13. Formation and demulsification mechanism of amino-modified Fe_3O_4@P(GMA-MMA-DVB) magnetic core-shell microsphere.
Modified from Ref. [6] with permission from John Wiley and Sons. Copyright (2015) The Chemical Society Located in Taipei & Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany.

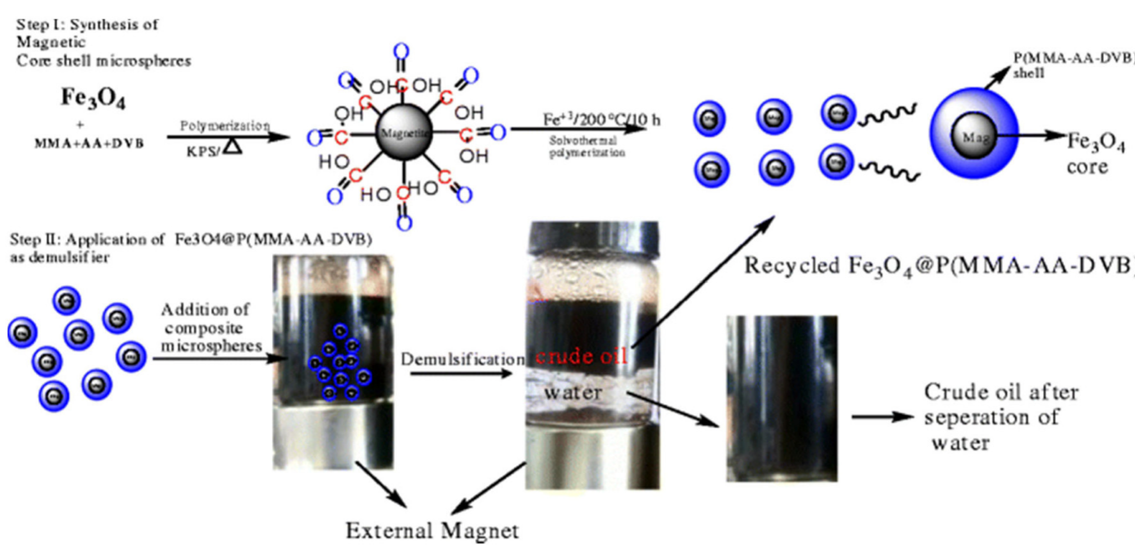


Fig. 14. Structure and formation mechanism of Fe_3O_4@P(MMA-AA-DVB) core-shell magnetic microspheres.
Reprinted from Ref. [5] with permission from Springer Nature. Copyright (2015) Springer Nature.

4) The contamination of aqueous media with oil is the most prominent issue to be faced with hostility with the "oil removing" tag. This issue is more serious in the oil fields where more thick and viscous oil-water emulsions destabilization is the daily task. For effective remediation of this issue, it is required to develop a technology for the preparation of more engineered and porous magnetic hybrid materials with high water affinity, super oleophobicity, low surface energy and air superoleophobicity for the separation of thick emulsions.
5) The design and synthesis of magnetic hybrid materials with effective oil-water separation efficiency and reusability has been achieved, but the improvement in the speed of separation is still

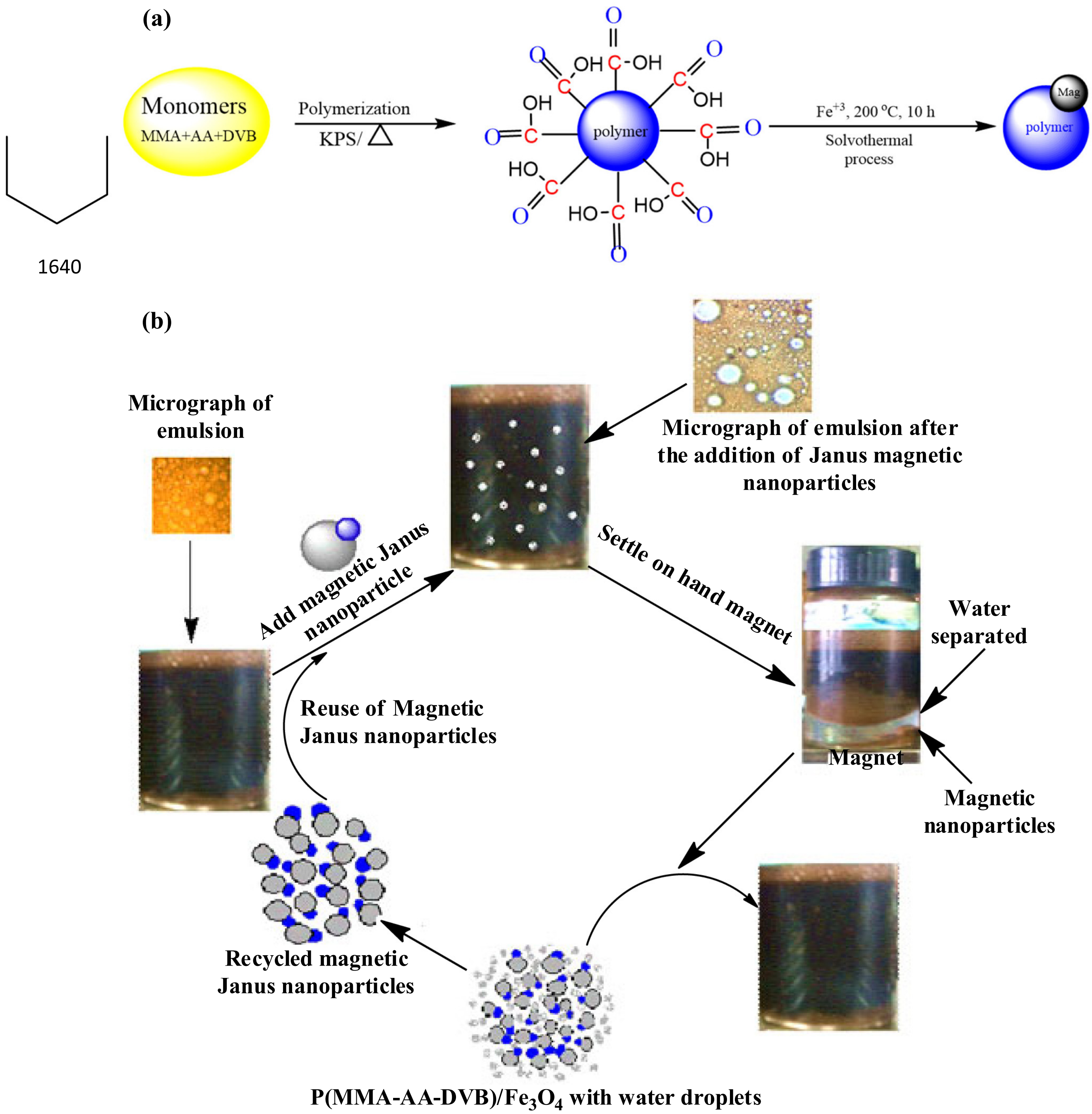


Fig. 15. (a) Synthetic procedures of Janus magnetic composite microspheres and (b) demulsification and recycling of P(MMA-AA-DVB)/Fe_3O_4 Janus magnetic composite microspheres. Reprinted from Ref. [3] with permission from Elsevier. Copyright (2014) Elsevier Ltd.

a desire. One of the possible solutions is the separation under high pressure. Therefore, rapid and efficient materials with pressure resistance and super-wettability properties should be developed. Finally yet importantly, the shape and surface morphology of the separation smart magnetic material is more important, which should be prevented from damage caused by the external environment, i.e. impact of liquid flow, mechanical stress, high pressure, etc. This condition is more important in the case of structured materials like porous adsorbent and fibrous membranes. In this case, materials of polymers or composites of magnetic-polymer exhibit excellent mechanical strength and hopefully will solve this problem. The synthesis and fabrication of polymer or inorganic-polymer (magnetic composite) separation materials are combined with the mass production problem at a large scale, so the development of cost-effective and simple methods are urgently required. Challenges are always at the front desk phenomenon, which motivates future achievements and us to fight. Advancement in polymer and material science holds the responsibility of composition, morphology and tunable design of smart materials targeted to meet the demand in the field of separation. The previous research work specifically focused on the synthesis of magnetic materials with smart surfaces through the functionalization of the targeted substrate with some smart polymers. If we can fabricate some new magnetic materials

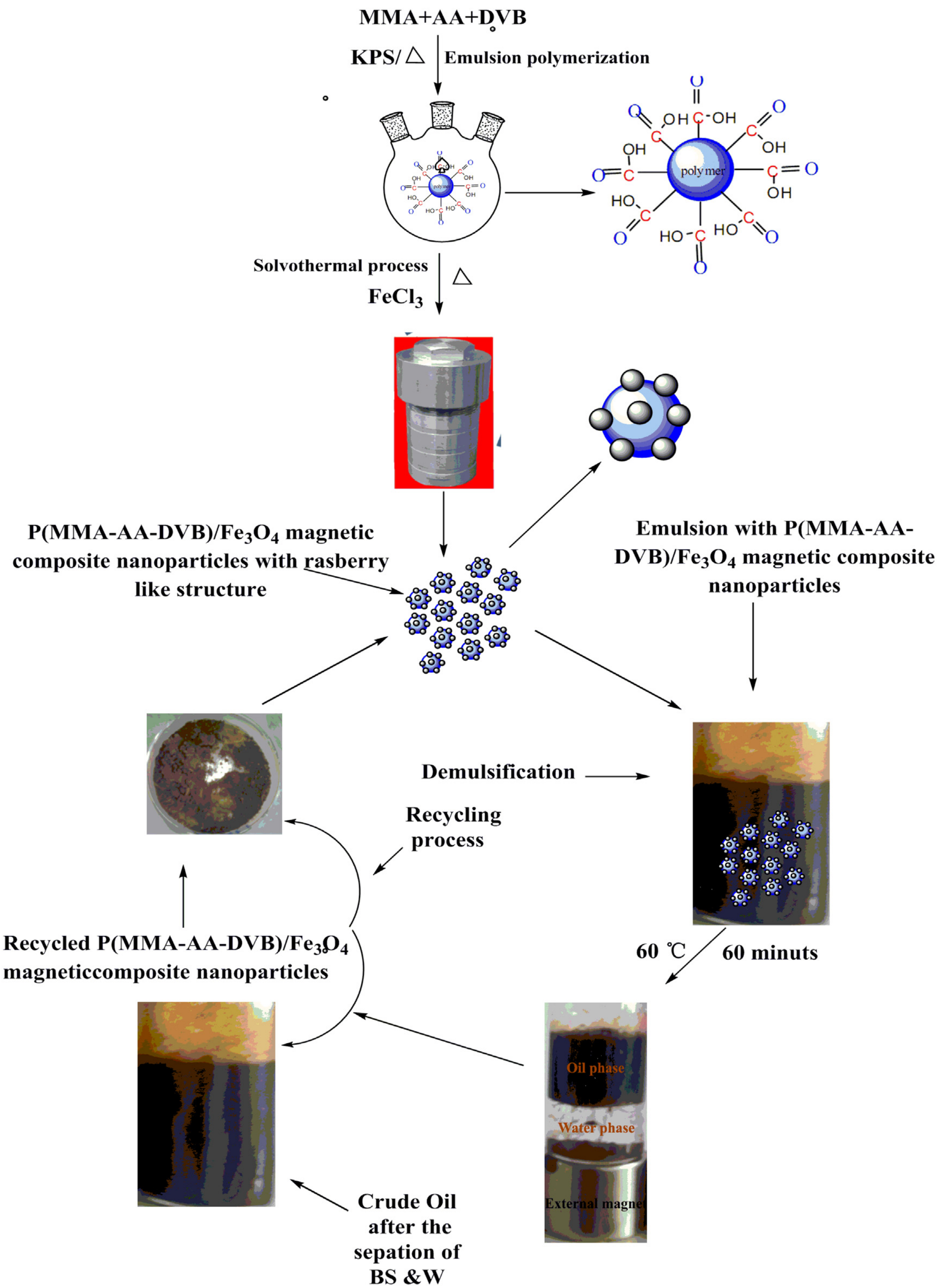


Fig. 16. Procedures are explained the process of synthesis, demulsification and recycling of raspberry like P(MMA-AA-DVB)/Fe_3O_4 magnetic composite nanoparticles. Reprinted from Ref. [4] with permission from Elsevier. Copyright (2015) Elsevier B.V.

with both smart polymer and smart surface, this may create a super-smart material with the super-smart application. In the present era, some new and facile materials with tunable and smart surfaces and chemistry have been developed. Due to the high demulsification efficiency and good reusability, the separation regulated through wettability shows more applications and advantages over the conventional methods used for separation, which may have a promising perspective in the field of oil wastewater treatment including demulsification of oil-water emulsion.

Declaration of competing interest

The authors report no conflict of interest in any capacity, i.e., competing or financial.

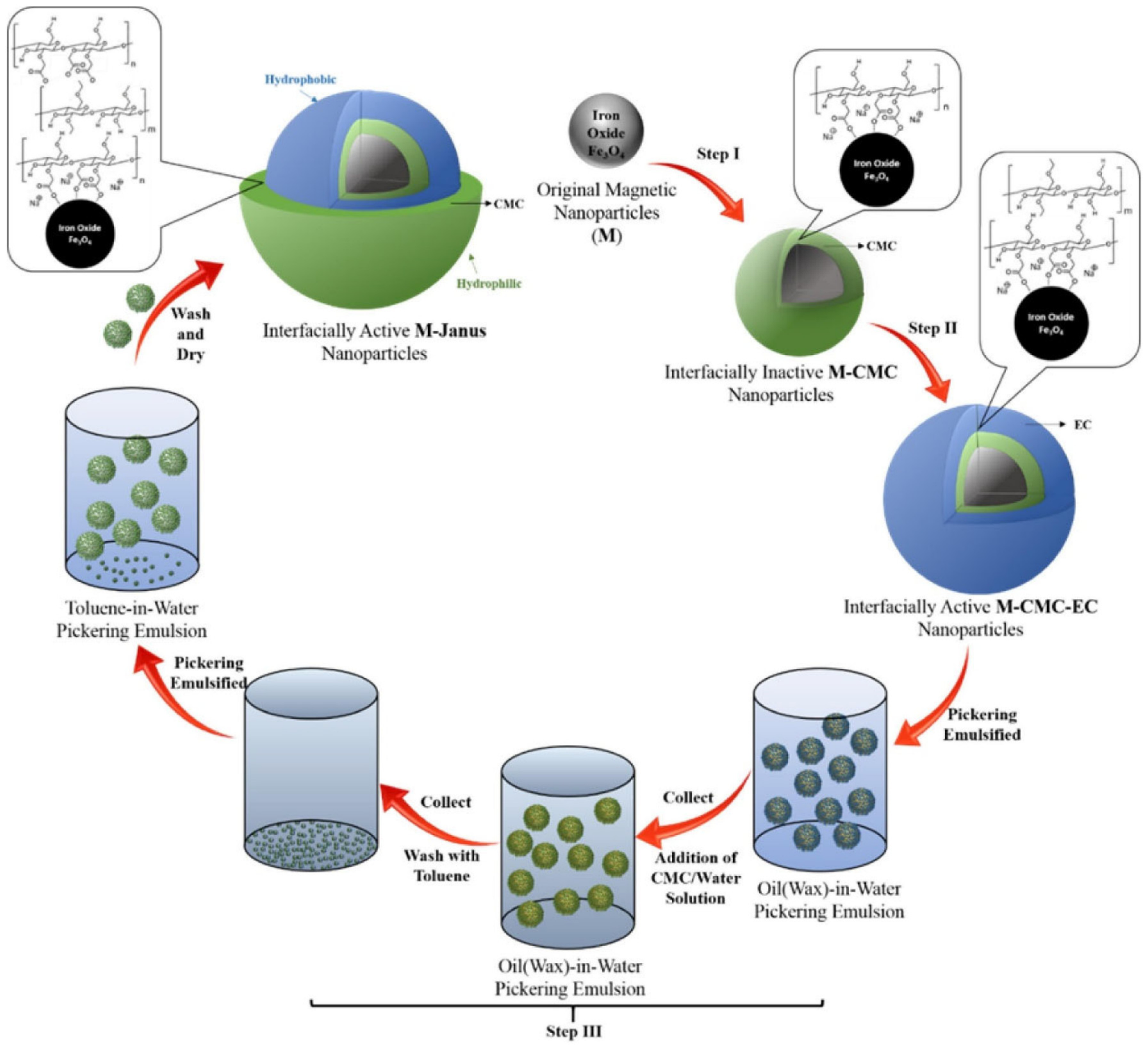


Fig. 17. Synthesis and demulsification procedures of M-Janus nanoparticles.
Reprinted from Ref. [231] with permission from Elsevier. Copyright (2019) Elsevier B.V.

Acknowledgments

All authors are thankful to their representative universities/institutes for the support and services used in this study.

References

[1] J. Tian, B. Huang, W. Zhang, Precise self-assembly and controlled catalysis of thermoresponsive core–satellite multicomponent hybrid nanoparticles, Langmuir 35 (1) (2018) 266–275.
[2] N. Ali, B. Zhang, H. Zhang, et al., Key synthesis of magnetic Janus nanoparticles using a modified facile method, Particuology 17 (2014) 59–65.
[3] N. Ali, B. Zhang, H. Zhang, et al., Novel Janus magnetic microparticle synthesis and its applications as a demulsifier for breaking heavy crude oil and water emulsion, Fuel 141 (2015) 258–267.
[4] N. Ali, B. Zhang, H. Zhang, et al., Interfacially active and magnetically responsive composite nanoparticles with raspberry-like structure; synthesis and its applications for heavy crude oil/water separation, Colloids Surf. A Physicochem. Eng. Asp. 472 (2015) 38–49.
[5] N. Ali, Z. Baoliang, H. Zhang, et al., Iron oxide-based polymeric magnetic microspheres with a core shell structure: from controlled synthesis to demulsification applications, J. Polym. Res. 22 (11) (2015) 219.
[6] N. Ali, B. Zhang, H. Zhang, et al., Monodispers and multifunctional magnetic composite core shell microspheres for demulsification applications, J. Chin. Chem. Soc. 62 (8) (2015) 695–702.
[7] B. Sarkar, P. Alexandridis, Block copolymer–nanoparticle composites: structure, functional properties, and processing, Prog. Polym. Sci. 40 (2015) 33–62.
[8] M. Molina, M. Asadian-Birjand, J. Balach, et al., Stimuli-responsive nanogel composites and their application in nanomedicine, Chem. Soc. Rev. 44 (17) (2015) 6161–6186.
[9] V. Brunetti, L.M. Bouchet, M.C. Strumia, Nanoparticle-cored dendrimers: functional hybrid nanocomposites as a new platform for drug delivery systems, Nanoscale 7 (9) (2015) 3808–3816.
[10] J. Shi, Y. Jiang, X. Wang, et al., Design and synthesis of organic–inorganic hybrid capsules for biotechnological applications, Chem. Soc. Rev. 43 (15) (2014) 5192–5210.
[11] D.H. Park, S.J. Hwang, J.M. Oh, et al., Polymer–inorganic supramolecular nanohybrids for red, white, green, and blue applications, Prog. Polym. Sci. 38 (10−11) (2013) 1442–1486.
[12] M.S. Shim, Y.J. Kwon, Stimuli-responsive polymers and nanomaterials for gene delivery and imaging applications, Adv. Drug Deliv. Rev. 64 (11) (2012) 1046–1059.
[13] N. Ali, M. Bilal, A. Khan, F. Ali, H.M. Iqbal, Design, engineering and analytical perspectives of membrane materials with smart surfaces for efficient oil/water separation, TrAC Trends Anal. Chem. (2020), 115902. https://doi.org/10.1016/j.trac.2020.115902.
[14] M. Vallet-Regí, M. Colilla, B. González, Medical applications of organic–inorganic hybrid materials within the field of silica-based bioceramics, Chem. Soc. Rev. 40 (2) (2011) 596–607.
[15] T.N. Hoheisel, K. Hur, U.B. Wiesner, Block copolymer-nanoparticle hybrid self-assembly, Prog. Polym. Sci. 40 (2015) 3–32.
[16] F. Mammeri, E. Le Bourhis, L. Rozes, et al., Mechanical properties of hybrid organic–inorganic materials, J. Mater. Chem. 15 (35–36) (2005) 3787–3811.
[17] The Supramolecular Chemistry of Organic-Inorganic Hybrid Materials[M]. , John Wiley & Sons, 2010 531–545.
[18] K.T. Nguyen, Y. Zhao, Engineered hybrid nanoparticles for on-demand diagnostics and therapeutics, Acc. Chem. Res. 48 (12) (2015) 3016–3025.

[19] C. Sanchez, B. Julián, P. Belleville, et al., Applications of hybrid organic–inorganic nanocomposites, J. Mater. Chem. 15 (35–36) (2005) 3559–3592.
[20] Y. Mai, A. Eisenberg, Self-assembly of block copolymers, Chem. Soc. Rev. 41 (18) (2012) 5969–5985.
[21] Y. Liu, Y. Zhang, Z. Wang, et al., Building nanowires from micelles: hierarchical self-assembly of alternating amphiphilic glycopolypeptide brushes with pendants of high-mannose glycodendron and oligophenylalanine, J. Am. Chem. Soc. 138 (38) (2016) 12387–12394.
[22] B. Zhang, X. Lv, Z. An, Modular monomer with tunable solubility: synthesis of highly incompatible block copolymer nano-objects via RAFT aqueous dispersion polymerization, ACS Macro Lett. 6 (3) (2017) 224–228.
[23] H. Cui, Z. Chen, S. Zhong, K.L. Wooley, D.J. Pochan, Block copolymer assembly via kinetic control, Science 317 (2007) 647–650.
[24] T.I. Löbling, O. Borisov, J.S. Haataja, et al., Rational design of ABC triblock terpolymer solution nanostructures with controlled patch morphology, Nat. Commun. 7 (2016), 12097. .
[25] T. Tigges, A. Walther, Hierarchical self-assembly of 3D-printed lock-and-key colloids through shape recognition, Angew. Chem. Int. Ed. 55 (2016) 11261–11265.
[26] E. Rieger, J. Blankenburg, E. Grune, M. Wagner, K. Landfester, F.R. Wurm, Controlling the polymer microstructure in anionic polymerization by compartmentalization, Angew. Chem. Int. Ed. 57 (2018) 2483–2487.
[27] X. Hu, J. Hu, J. Tian, et al., Polyprodrug amphiphiles: hierarchical assemblies for shape-regulated cellular internalization, trafficking, and drug delivery, J. Am. Chem. Soc. 135 (46) (2013) 17617–17629.
[28] Z. Zhang, C. Zhou, H. Dong, et al., Solution-based fabrication of narrow-disperse ABC three-segment and Θ-shaped nanoparticles, Angew. Chem. Int. Ed. 55 (21) (2016) 6182–6186.
[29] K.V. Rao, D. Miyajima, A. Nihonyanagi, et al., Thermally bisignate supramolecular polymerization, Nat. Chem. 9 (11) (2017) 1133.
[30] J. Wen, L. Yuan, Y. Yang, et al., Self-assembly of monotethered single-chain nanoparticle shape amphiphiles, ACS Macro Lett. 2 (2) (2013) 100–106.
[31] M.J. Derry, L.A. Fielding, S.P. Armes, Polymerization-induced self-assembly of block copolymer nanoparticles via RAFT non-aqueous dispersion polymerization, Prog. Polym. Sci. 52 (2016) 1–18.
[32] K. Matyjaszewski, N.V. Tsarevsky, Nanostructured functional materials prepared by atom transfer radical polymerization, Nat. Chem. 1 (4) (2009) 276.
[33] P.A. Rupar, L. Chabanne, M.A. Winnik, et al., Non-centrosymmetric cylindrical micelles by unidirectional growth, Science 337 (6094) (2012) 559–562.
[34] N.J. Warren, S.P. Armes, Polymerization-induced self-assembly of block copolymer nano-objects via RAFT aqueous dispersion polymerization, J. Am. Chem. Soc. 136 (29) (2014) 10174–10185.
[35] X. Ye, C. Zhu, P. Ercius, S.N. Raja, B. He, M.R. Jones, M.R. Hauwiller, Y. Liu, T. Xu, A.P. Alivisatos, Structural diversity in binarys self-assembled from polymer-grafted nano-crystals, Nat. Commun. 6 (2015) 10052.
[36] R. Costi, A.E. Saunders, U. Banin, Colloidal hybrid nanostructures: a new type of functional material, Angew. Chem. Int. Ed. 49 (29) (2010) 4878–4897.
[37] A. Wolf, A. Walther, A.H.E. Müller, Janus triad: three types of nonspherical, nanoscale janus particles from one single triblock terpolymer, Macromolecules 44 (23) (2011) 9221–9229.
[38] T. Hao, X. Wu, L. Xu, L. Liu, W. Ma, H. Kuang, C. Xu, Ultrasensitive detection of prostate-specific antigen and thrombin based on gold-upconversion nanoparticle assembled pyramids, Small 13 (2017), 1603944. .
[39] C. Schmidtke, H. Kloust, N.G. Bastús, et al., A general route towards well-defined magneto-or fluorescent-plasmonic nanohybrids, Nanoscale 5 (23) (2013) 11783–11794.
[40] A. Li, L. Tang, D. Song, et al., A SERS-active sensor based on heterogeneous gold nanostar core–silver nanoparticle satellite assemblies for ultrasensitive detection of aflatoxinB1, Nanoscale 8 (4) (2016) 1873–1878.
[41] N. Gandra, A. Abbas, L. Tian, et al., Plasmonic planet–satellite analogues: hierarchical self-assembly of gold nanostructures, Nano Lett. 12 (5) (2012) 2645–2651.
[42] L.Y.T. Chou, K. Zagorovsky, W.C.W. Chan, DNA assembly of nanoparticle superstructures for controlled biological delivery and elimination, Nat. Nanotechnol. 9 (2) (2014) 148.
[43] R. Schreiber, J. Do, E.M. Roller, et al., Hierarchical assembly of metal nanoparticles, quantum dots and organic dyes using DNA origami scaffolds, Nat. Nanotechnol. 9 (1) (2014) 74.
[44] X. Xu, N.L. Rosi, Y. Wang, et al., Asymmetric functionalization of gold nanoparticles with oligonucleotides, J. Am. Chem. Soc. 128 (29) (2006) 9286–9287.
[45] L. Wu, U. Gleb, A. Boker, Fabrication of thermoresponsive plasmonic core—satellite nanoassemblies with a tunable Stoichi-ometry via surface-initiated reversible addition—fragmentation chain transfer polymerization from silica nanoparticles, Adv. Mater. Interfaces 4 (2017), 1700092. .
[46] F. Han, S.R.C. Vivekchand, A.H. Soeriyadi, et al., Thermoresponsive plasmonic core–satellite nanostructures with reversible, temperature sensitive optical properties, Nanoscale 10 (9) (2018) 4284–4290.
[47] E.G. Kelley, J.N.L. Albert, M.O. Sullivan, et al., Stimuli-responsive copolymer solution and surface assemblies for biomedical applications, Chem. Soc. Rev. 42 (17) (2013) 7057–7071.
[48] M.V.G. Paixão, R.C.S. da Luz, R. de Carvalho Balaban, Thermoresponsive polymer brushes on magnetic chitosan microspheres: synthesis, characterization and application in oily water of high salinity, J. Mol. Liq. 286 (2019), 110792. .
[49] Hira Zaman, Nisar Ali, Anwar ul Haq Ali Shah, Xiaoyan Gao, Shizhong Zhang, Kun Hong, Effect of pH and salinity on stability and dynamic properties of magnetic composite amphiphilic demulsifier molecules at the oil-water interface, J. Mol. Liq. 290 (2019), 111186. .
[50] N. Ali, H. Zaman, M. Bilal, M.S. Nazir, H.M. Iqbal, Environmental perspectives of interfacially active and magnetically recoverable composite materials–a review, Sci. Total Environ. 670 (2019) 523–538.
[51] A. Khan, N. Ali, M. Bilal, S. Malik, S. Badshah, H. Iqbal, Engineering functionalized chitosan-based sorbent material: characterization and sorption of toxic elements, Appl. Sci. 9 (23) (2019) 5138.
[52] N. Ali, A. Khan, M. Bilal, S. Malik, S. Badshah, H. Iqbal, Chitosan-based biocomposite modified with thiocarbamate moiety for decontamination of cations from the aqueous media, Molecules 25 (1) (2020) 226.
[53] F. Liu, M.W. Urban, Recent advances and challenges in designing stimuli-responsive polymers, Prog. Polym. Sci. 35 (1–2) (2010) 3–23.
[54] S. Wu, J. Dzubiella, J. Kaiser, et al., Thermosensitive Au-PNIPA yolk–shell nanoparticles with tunable selectivity for catalysis, Angew. Chem. Int. Ed. 51 (9) (2012) 2229–2233.
[55] D.D. Díaz, D. Kühbeck, R.J. Koopmans, Stimuli-responsive gels as reaction vessels and reusable catalysts, Chem. Soc. Rev. 40 (1) (2011) 427–448.
[56] Z. Ge, S. Liu, Functional block copolymer assemblies responsive to tumor and intracellular microenvironments for site-specific drug delivery and enhanced imaging performance, Chem. Soc. Rev. 42 (17) (2013) 7289–7325.
[57] W. Wu, W. Dai, X. Zhao, et al., Synthesis, self-assembly and drug release behaviors of reduction-labile multi-responsive block miktobrush quaterpolymers with linear and V-shaped grafts, Polym. Chem. 9 (15) (2018) 1947–1960.
[58] K. Liu, R. Xing, Q. Zou, et al., Simple peptide-tuned self-assembly of photosensitizers towards anticancer photodynamic therapy, Angew. Chem. Int. Ed. 55 (9) (2016) 3036–3039.
[59] G. Yu, R. Zhao, D. Wu, et al., Pillar arene-based amphiphilic supramolecular brush copolymers: fabrication, controllable self-assembly and application in self-imaging targeted drug delivery, Polym. Chem. 7 (40) (2016) 6178–6188.
[60] Y. Tian, B. Su, L. Jiang, Interfaces: interfacial material system exhibiting Superwettability (Adv. Mater. 40/2014), Adv. Mater. 26 (40) (2014) 6871.
[61] S. Wang, K. Liu, X. Yao, et al., Bioinspired surfaces with superwettability: new insight on theory, design, and applications, Chem. Rev. 115 (16) (2015) 8230–8293.
[62] M. Liu, S. Wang, L. Jiang, Nature-inspired superwettability systems, Nat. Rev. Mater. 2 (7) (2017), 17036. .
[63] B. Bhushan, Y.C. Jung, Natural and biomimetic artificial surfaces for superhydrophobicity, self-cleaning, low adhesion, and drag reduction, Prog. Mater. Sci. 56 (1) (2011) 1–108.
[64] L. Wen, Y. Tian, L. Jiang, Bioinspired super-wettability from fundamental research to practical applications[J], Angew. Chem. Int. Ed. 54 (11) (2015) 3387–3399.
[65] Z. Xue, Y. Cao, N. Liu, et al., Special wettable materials for oil/water separation, J. Mater. Chem. A 2 (8) (2014) 2445–2460.
[66] Y. Zhu, D. Wang, L. Jiang, et al., Recent progress in developing advanced membranes for emulsified oil/water separation, NPG Asia Materials 6 (5) (2014) e101.
[67] G. Kwon, E. Post, A. Tuteja, Membranes with selective wettability for the separation of oil–water mixtures, MRS Communications 5 (3) (2015) 475–494.
[68] Q. Ma, H. Cheng, A.G. Fane, R. Wang, H. Zhang, Recent development of advancedmaterials with special wettability for selective oil/water separation, Small 12 (2016) 2186–2202.
[69] R.K. Gupta, G.J. Dunderdale, M.W. England, A. Hozumi, Oil/water separation techniques: a review of recent progresses and future directions, J. Mater. Chem. A 5 (2017) 16025–16058.
[70] L. Feng, Z. Zhang, Z. Mai, Y. Ma, B. Liu, L. Jiang, et al., A super-hydrophobic and super-oleophilic coating mesh film for the separation of oil and water, Angew. Chem. Int. Ed. 43 (2004) 2012–2014.
[71] M. Liu, S. Wang, Z. Wei, Y. Song, L. Jiang, Bioinspired design of asuperoleophobic and low adhesive water/solid interface, Adv. Mater. 21 (2009) 665–669.
[72] Z. Xue, S. Wang, L. Lin, L. Chen, M. Liu, L. Feng, et al., A novel superhydrophilic and underwater superoleophobic hydrogel-coated mesh for oil/water separation, Adv. Mater. 23 (2011) 4270–4273.
[73] W. Yuan, Z. Zhao, J. Yuan, et al., Synthesis of pH-and temperature-responsive chitosan-graft-poly [2-(N, N-dimethylamino) ethyl methacrylate] copolymer and gold nanoparticle stabilization by its micelles, Polym. Int. 60 (2) (2011) 194–201.
[74] D.C. Maia Filho, J.B.V.S. Ramalho, L.S. Spinelli, et al., Aging of water-in-crude oil emulsions: effect on water content, droplet size distribution, dynamic viscosity and stability, Colloids Surf. A Physicochem. Eng. Asp. 396 (2012) 208–212.
[75] R. Martínez-Palou, M. de Lourdes Mosqueira, B. Zapata-Rendón, et al., Transportation of heavy and extra-heavy crude oil by pipeline: a review, J. Pet. Sci. Eng. 75 (3–4) (2011) 274–282.
[76] R. Martínez-Palou, J. Reyes, R. Cerón-Camacho, et al., Study of the formation and breaking of extra-heavy-crude-oil-in-water emulsions—a proposed strategy for transporting extra heavy crude oils, Chem. Eng. Process. Process Intensif. 98 (2015) 112–122.
[77] A.A.A.A. Azim, A.R.M. Abdul-Raheim, R.K. Kamel, et al., Demulsifier systems applied to breakdown petroleum sludge, J. Pet. Sci. Eng. 78 (2) (2011) 364–370.
[78] L. Hong, G. Sun, J. Cai, et al., One-step formation of w/o/w multiple emulsions stabilized by single amphiphilic block copolymers, Langmuir 28 (5) (2012) 2332–2336.
[79] A.Y. El Naggar, E.A. Saad, H.O. Elmoher, Petroleum cuts as solvent extractor for oil recovery from petroleum sludge, J. Pet. Technol. Altern. Fuel 1 (1) (2010) 10–19.
[80] E.R. Shperber, T.N. Bokovikova, D.R. Shperber, Sources of formation and methods of utilization of oil sludges, Chem. Technol. Fuels Oils 47 (2) (2011) 160.
[81] A. Drelich, F. Gomez, D. Clausse, et al., Evolution of water-in-oil emulsions stabilized with solid particles: influence of added emulsifier, Colloids Surf. A Physicochem. Eng. Asp. 365 (1–3) (2010) 171–177.
[82] E.J. Ekott, E.J. Akpabio, A review of water-in-crude oil emulsion stability, destabilization and interfacial rheology, J. Eng. Appl. Sci. 5 (6) (2010) 447–452.

[83] E. Fredrick, P. Walstra, K. Dewettinck, Factor's governing partial coalescence in oil in water emulsions, Adv. Colloid Interf. Sci. 153 (1–2) (2010) 30–42.
[84] J.M. Gutiérrez, C. González, A. Maestr, I. Sole, C.M. Pey, J. Nolla, Nano emulsions: new applications and optimization of their preparation, Curr. Opin. Colloid Interface Sci. 13 (4) (2008) 245–251.
[85] C.L. Yang, Electrochemical coagulation for oily water demulsification, Sep. Purif. Technol. 54 (3) (2007) 388–395.
[86] C.C. de Morais, M.C. Chiu, R.C. Basso, A.P.B. Ribeiro, L.A.G. Gonçalves, L.A. Viotto, State of art of the application of membrane technology to vegetable oils: a review, Food Res. Int. 42 (5–6) (2009) 536–550.
[87] E.E. Isaacs, H. Huang, A.J. Babchin, R.S. Chow, Electroacoustic method for monitoring the coalescence of water in oil emulsions, Colloids Surf. 46 (2) (1990) 177–192.
[88] A.P. Sullivan, P.K. Kilpatrick, The effects of inorganic solid particles on water and crude oil emulsion stability, Ind. Eng. Chem. Res. 41 (2002) 3389–3404.
[89] L. Liggieri, M. Ferrari, F. Ravera, A. Passerone, R. Miller, O. Minster, B. Schürmann, G. Loglio, Adsorption dynamics interfacial elasticity and emulsion stability, Proceedings of the First International Symposium, 454, European Space Agency, ESA SP 2001, pp. 133–139.
[90] D. Langevin, S. Poteau, I. Henaut, J.F. Argillier, Crude oil emulsion properties and their application to heavy oil transportation, Oil Gas Sci. Technol. 59 (5) (2004) 511–521.
[91] D. Arla, A. Sinquin, T. Palermo, et al., Influence of pH and water content on the type and stability of acidic crude oil emulsions, Energy Fuel 21 (3) (2007) 1337–1342.
[92] A.A.A.A. Azim, M.E.S. Abdel-Raouf, A.R.M. Abdel-Raheim, et al., Sugar-based ethoxylated amine surfactants as demulsifiers for crude oil emulsions: 2-demulsification of different types of crudes, Braz. J. Pet. Gas 4 (4) (2010).
[93] A. Bera, A. Mandal, B.B. Guha, Synergistic effect of surfactant and salt mixture on interfacial tension reduction between crude oil and water in enhanced oil recovery, J. Chem. Eng. Data 59 (1) (2013) 89–96.
[94] D. Langevin, S. Poteau, I. Hénaut, et al., Crude oil emulsion properties and their application to heavy oil transportation, Oil Gas Sci. Technol. 59 (5) (2004) 511–521.
[95] R. Martínez-Palou, R. Cerón-Camacho, B. Chávez, et al., Demulsification of heavy crude oil-in-water emulsions: a comparative study between microwave and thermal heating, Fuel 113 (2013) 407–414.
[96] K. Alinezhad, M. Hosseini, K. Movagarnejad, M. Salehi, Experimental and modeling approach to study separation of water in crude oil emulsion under non-uniform electrical field, Korean J. Chem. Eng. 27 (1) (2010) 198–205.
[97] A.H. Nour, R.M. Yunus, Z. Jemaat, Characterization and demulsification of water-in-crude oil emulsions, J. Appl. Sci. 7 (10) (2007) 1437–1441.
[98] V.J. Verruto, R.K. Le, P.K. Kilpatrick, Adsorption and molecular rearrangement of amphoteric species at oil water interfaces, J. Phys. Chem. B 113 (42) (2009) 13788–13799.
[99] S. Less, A. Hannisdal, E. Bjorklund, J. Sjöblom, Electrostatic destabilization of water in crude oil emulsions: application to a real case and evaluation of the Aibel VIEC technology, Fuel 87 (12) (2008) 2572–2581.
[100] E.T. Igunnu, G.Z. Chen, Produced water treatment technologies, Int. J. Low-Carbon Technol. 9 (3) (2012) 157–177.
[101] F. Merv, M. Fingas, Water in oil emulsions: formation and prediction, J. Pet. Sci. Res. 3 (1) (2014) 214–218.
[102] M. Fingas, B. Fieldhouse, Studies on water in oil products from crude oils and petroleum products, Mar. Pollut. Bull. 64 (2011) 272–283.
[103] P. Tchoukov, F. Yang, Z. Xu, et al., Role of asphaltenes in stabilizing thin liquid emulsion films, Langmuir 30 (11) (2014) 3024–3033.
[104] D. Pradilla, S. Simon, J. Sjöblom, Mixed interfaces of asphaltenes and model demulsifiers part I: adsorption and desorption of single components, Colloids Surf. A Physicochem. Eng. Asp. 466 (2015) 45–56.
[105] Q. An, Y. Zhang, K. Lv, et al., A facile method to fabricate functionally integrated devices for oil/water separation, Nanoscale 7 (10) (2015) 4553–4558.
[106] J. Czarnecki, Stabilization of water in crude oil emulsions. Part 2, Energy Fuel 23 (3) (2008) 1253–1257.
[107] H.W. Yarranton, D.M. Sztukowski, P. Urrutia, Effect of interfacial rheology on model emulsion coalescence: I. Interfacial rheology, J. Colloid Interface Sci. 310 (1) (2007) 246–252.
[108] N. Carnahan, J.L. Salager, R. Anton, Effect of resins on stability of asphaltenes, Offshore Technology Conference. Houston, Texas. (2007) 1–9.
[109] P.C.S. Zorzenão, R.M. Mariath, F.E. Pinto, et al., Asphaltenes subfractions extracted from Brazilian vacuum residue: chemical characterization and stabilization of model water-in-oil (W/O) emulsions, J. Pet. Sci. Eng. 160 (2018) 1–11.
[110] Y. Chevalier, M.A. Bolzinger, Emulsions stabilized with solid nanoparticles: Pickering emulsions, Colloids Surf. A Physicochem. Eng. Asp. 439 (2013) 23–34.
[111] D.E. Dmitriev, A.K. Golovko, Modelling the molecular structures of petroleum resins and asphaltenes and their thermodynamic stability calculation, Chem. Sustain. Dev. 18 (2010) 171–180.
[112] F. Saliu, R. Della Pergola, Organic bases, carbon dioxide and naphthenic acids interactions. Effect on the stability of petroleum crude oil in water emulsions, J. Pet. Sci. Eng. 163 (2018) 177–184.
[113] D.M. Sztukowski, H.W. Yarranton, Oilfield solids and water in oil emulsion stability, J. Colloid Interface Sci. 285 (2) (2005) 821–833.
[114] H. Radnia, A.R.S. Nazar, A. Rashidi, Effect of asphaltene on the emulsions stabilized by graphene oxide: a potential application of graphene oxide in enhanced oil recovery, J. Pet. Sci. Eng. 175 (2019) 868–880.
[115] X. Mao, L. Gong, L. Xie, et al., Novel Fe_3O_4 based superhydrophilic core-shell microspheres for breaking asphaltenes-stabilized water-in-oil emulsion, Chem. Eng. J. 358 (2019) 869–877.
[116] G. Chen, G. He, Separation of water and oil from water in oil emulsion by freeze/thaw method, Sep. Purif. Technol. 31 (1) (2003) 83–89.
[117] J.S. Eow, M. Ghadiri, Electrostatic enhancement of coalescence of water droplets in oil: a review of the technology, Chem. Eng. J. 85 (2–3) (2002) 357–368.
[118] Y. Chizawa, Y. Miyagawa, M. Yoshida, et al., Effect of crystallization of oil phase on the destabilization of O/W emulsions containing vegetable oils with low melting points, Colloids Surf. A Physicochem. Eng. Asp. 582 (2019), 123824. .
[119] R. Zolfaghari, A. Fakhru'l-Razi, L.C. Abdullah, et al., Demulsification techniques of water-in-oil and oil-in-water emulsions in petroleum industry, Sep. Purif. Technol. 170 (2016) 377–407.
[120] A.N. Dimitrov, D.I. Yordanov, P.S. Petkov, Study on the effect of demulsifers on crude oil and petroleum product, Int. J. Environ. Res. 6 (2) (2012) 435–442.
[121] T. Young, An essay on the cohesion of fluids, Philos. Trans. R. Soc. Lond. 95 (1805) 65–87.
[122] Z. Wang, M. Elimelech, S. Lin, Environmental applications of interfacial materials with special wettability, Environ. Sci. Technol. 50 (2016) 2132–2150.
[123] Y. Yuan, T.R. Lee, Contact Angle and Wetting Properties, Surface Science Techniques, Springer Berlin Heidelberg, 2013 3–34.
[124] L. Feng, S. Li, Y. Li, H. Li, L. Zhang, J. Zhai, Y. Song, B. Liu, L. Jiang, D. Zhu, Superhydrophobic surfaces: from natural to artificial, Adv. Mater. 14 (2002) 1857–1860.
[125] M. Nosonovsky, Slippery when wetted, Nature 477 (2011) 412.
[126] H.J. Lee, J.R. Owens, Motion of liquid droplets on a superhydrophobic oleophobic surface, J. Mater. Sci. 46 (2011) 69–76.
[127] S. Pan, A.K. Kota, J.M. Mabry, A. Tuteja, Superomniphobic surfaces for effective chemical shielding, J. Am. Chem. Soc. 135 (2013) 578–581.
[128] J. Yong Chae, B. Bharat, Contact angle, adhesion and friction properties of micro-and nanopatterned polymers for superhydrophobicity, Nanotechnology 17 (2006) 4970–4980.
[129] F. Xia, L. Feng, S. Wang, T. Sun, W. Song, W. Jiang, L. Jiang, Dual-responsive surfaces that switch between superhydrophilicity and superhydrophobicity, Adv. Mater. 18 (2006) 432–436.
[130] W. Ma, H. Xu, A. Takahara, Substrate-independent underwater superoleophobic surfaces inspired by fish-skin and mussel-adhesives, Adv. Mater. Interfaces 1 (2014) 1–5.
[131] J. Yong, F. Chen, Q. Yang, X. Hou, Femtosecond laser controlled wettability of solid surfaces, Soft Matter 11 (2015) 8897–8906.
[132] E. Zhang, Z. Cheng, T. Lv, Y. Qian, Y. Liu, Anti-corrosive hierarchical structured copper mesh film with superhydrophilicity and underwater low adhesive superoleophobicity for highly efficient oil/water separation, J. Mater. Chem. A 3 (2015) 13411–13417.
[133] F. Zhang, S. Gao, Y. Zhu, J. Jin, Alkaline-induced superhydrophilic/underwater superoleophobic polyacrylonitrile membranes with ultralow oil-adhesion for high-efficient oil/water separation, J. Membr. Sci. 513 (2016) 67–73.
[134] K. Huang, J. Chen, S.R. Nugen, J.M. Goddard, Hybrid antifouling and antimicrobial coatings prepared by electroless co-deposition of fluoropolymer and cationic silica nanoparticles on stainless steel: efficacy against listeria monocytogenes, ACS Appl. Mater. Interfaces 8 (2016) 15926–15936.
[135] J.N. Israelachvili, Intermolecular and Surface Forces, Third Academic Press, USA, 2011.
[136] Y. Yuan, T.R. Lee, Contact angle and wetting properties, Surface science techniques, Springer (2013) 3–34.
[137] A. Marmur, Wetting on hydrophobic rough surfaces: to be heterogeneous or not to be? Langmuir 19 (2003) 8343–8348.
[138] G. McHaleCassie, Wenzel: were they really so wrong? Langmuir 23 (2007) 8200–8205.
[139] M. Bilal, S. Mehmood, T. Rasheed, H. Iqbal, Bio-catalysis and biomedical perspectives of magnetic nanoparticles as versatile carriers, Magnetochemistry 5 (3) (2019) 42.
[140] J. Pieracci, J.V. Crivello, G. Belfort, UV-assisted graft polymerization of N-Vinyl-2-pyrrolidinone onto poly(ether sulfone) ultrafiltration membranes using selective UV wavelengths, Chem. Mater. 14 (2002) 256–265.
[141] S. Piletsky, H. Matuschewski, U. Schedler, A. Wilpert, E. Piletska, T.A. Thirle, M. Ulbricht, Surface functionalization of porous polypropylene membranes with molecularly imprinted polymers by photo graft copolymerization in water, Macromolecules 33 (2000) 3092–3098.
[142] D.S. Wavhal, E.R. Fisher, Membrane surface modification by plasma-induced polymerization of acrylamide for improved surface properties and reduced protein fouling, Langmuir 19 (2003) 79–85.
[143] M. Ulbricht, H. Yang, Porous polypropylene membranes with different carboxyl polymer brush layers for reversible protein binding via surface initiated graft copolymerization, Chem. Mater. 17 (2005) 2622–2631.
[144] N. Singh, S.M. Husson, B. Zdyrko, I. Luzinov, Surface modification of microporous PVDF membranes by ATRP, J. Membr. Sci. 262 (2005) 81–90.
[145] J.P. Chen, Y.P. Chiang, Surface modification of non-woven fabric by DC pulsed plasma treatment and graft polymerization with acrylic acid, J. Membr. Sci. 270 (2006) 212–220.
[146] S. Michielsen, The effect of grafted polymeric lubricant molecular weight on the frictional characteristics of nylon 6, 6 fibers, J. Appl. Polym. Sci. 73 (1999) 129–136.
[147] Z. Hongjie, I. Yoshihiro, pH control of transport through a porous membrane self-assembled with a poly(acrylic acid) loop brush, Langmuir 17 (2001) 8336–8340.
[148] V. Rotello, Microspheres: Building Blocks for Nanotechnology [M], Springer, 2003.
[149] L.H. Tan, S.X. Xing, T. Chen, G. Chen, X. Huang, H. Zhang, H.Y. Chen, Fabrication of polymer nanocavities with tailored openings, ACS Nano 3 (2009) 3469–3474.
[150] R. Erhardt, A. Boker, H. Zettl, H. Kaya, W. Pyckhout-Hintzen, G. Krausch, V. Abetz, A.H.E. Mueller, Polymeric nano-particles of flower-like structure and applications, Macromolecules 34 (2001) 1069–1075.

[151] Z. Xu, J. Wang, L. Shen, D. Men, Y. Xu, Microporous polypropylene hollow fiber membrane: part I. Surface modification by the graft polymerization of acrylic acid, J. Membr. Sci. 196 (2002) 221–229.
[152] D.E. Bergbreiter, A. Bandella, pH and solvent responsive reactivity of surface-grafted polyethylene films, J. Am. Chem. Soc. 117 (1995) 10579–10580.
[153] L.L. Zhou, J.Y. Yuan, Y. Wei, Core-shell structural magnetic hybrid microspheres: from the controlled synthesis to biomedical applications, J. Mater. Chem. 21 (2011) 2823–2840.
[154] Z.L. Liu, Z.H. Ding, K.L. Yao, X. Chen, K.L. Yao, J. Tao, G.H. Du, Q.H. Lu, X. Wang, F.L. Gong, Preparation and characterization of polymer-coated core-shell structured magnetic microbeads, J. Magn. Magn. Mater. 265 (2003) 98–105.
[155] Z. Li, L. Qiang, S. Zhong, H. Wang, X. Cui, Synthesis and characterization of monodisperse magnetic Fe_3O_4@BSA core shell microspheres, Colloids Surf. A Physicochem. Eng. Asp. 436 (2013) 1145–1151.
[156] W.C. Law, K.T. Yong, I. Roy, G. Xu, H. Ding, E.J. Bergey, Aqueous-phase synthesis of highly luminescent CdTe/ZnTe core/shell quantum dots optimized for targeted bio imaging, J. Phys. Chem. C 112 (112) (2008) 7972–7977.
[157] N. Soundarya, Y. Zhang, Use of core-shell structured microspheres for biomedical applications, Recent Patents Biomed. Eng. 1 (2010) 34–42.
[158] A. Perro, S. Reculusa, F. Pereira, M.H. Delville, C. Mingotaud, E. Duguet, E. Bourgeat-Lami, S. Ravaine, Towards large amounts of Janus microspheres though a protection deprotection route, Chem. Commun. (2005) 5542–5543.
[159] W.S. Ho C C, Chen, T.Y. Shie, J.N. Lin, C. Kuo, Novel fabrication of Janus particles from the surface of electrospun polymer, Langmuir 24 (2008) 5663–5666.
[160] K.H. Roh, D.C. Martin, J. Lahann, Biphasic Janus particles with nanoscale anisotropy, Nat. Mater. 4 (2005) 759–763.
[161] W. Andreas, Axel H.E. Muller, Janus particles, Soft Matter 4 (2008) 663–668.
[162] J.P. Ge, Y.X. Hu, T.R. Zhang, Y.D. Yin, Fabrication and assembly of magneto responsive, anisotropic, and hybrid microparticles of variable size and shape, J. Am. Chem. Soc. 129 (2007) 8974.
[163] D. Horak, M. Babic, H. Mackova, M.J. Benes, Preparation and properties of magnetic nano and microsized particles for biological and environmental separations, J. Sep. Sci. 30 (2007) 1751–1772.
[164] A. Khan, A.M. El-Toni, M. Alsalhi, S.A. Abdullah, M. Alhoshan, Preparation of magnetic polyacrylonitrile core shell nanospheres by the miniemulsion polymerization method, Mater. Lett. 76 (2012) 141–143.
[165] C. Petchthanasombat, T. Tiensing, P. Sunintaboon, Synthesis of zinc oxide encapsulated poly(methyl methacrylate)-chitosan core-shell hybrid particles and their electrochemical property, J. Colloid Interface Sci. 369 (2012) 52–57.
[166] C. Tao, Y. Miaoxin, W. Xinjiao, H.T. Li, C. Hongyu, Controlled assembly of eccentrically encapsulated gold microspheres, J. Am. Chem. Soc. 130 (36) (2008) 11858–11859.
[167] O. Akira, C.C. Eun, H.C. Pedro, A. Leslie, O. Bunsho, X. Younan, B. Xu, A facile synthesis of asymmetric hybrid colloidal particles, J. Am. Chem. Soc. 131 (4) (2009) 1352–1353.
[168] H. Gu, R. Zheng, X. Zhang, B. Xu, Facile one-pot synthesis of bifunctional heterodimers of microspheres: a conjugate of quantum dot and magnetic microspheres, J. Am. Chem. Soc. 126 (18) (2004) 5664–5665.
[169] C.G. Sharon, J.S. Michael, Anisotropy of building blocks and their assembly into complex structures, Nat. Mater. 6 (2007) 557–562.
[170] Sharon C. Glotzer, Self-assembly of patchy particles, Nano Lett. 4 (8) (2004) 1407–1413.
[171] S. Jiang, S. Granick, Janus balance of amphiphilic colloidal particles, J. Chem. Phys. 127 (2007) 161102–161104.
[172] A. Giacometti, F. Lado, J. Largo, G. Pastore, F. Sciortino, Effects of patch size and number within a simple model of patchy colloids, J. Chem. Phys. 132 (2010) 174110–174115.
[173] L. Shuqiang, L. Naixu, Y. Shanbo, L. Fangyuan, Z. Jiancheng, The synthesis of a novel magnetic demulsifier and its application for the demulsification of oil-charged industrial wastewaters, J. Mater. Chem. A 2 (2014) 94–99.
[174] A.H. Lu, E.L. Salabas, F. Schüth, Magnetic microspheres: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed. 46 (2007) 1222–1244.
[175] M. Kokate, K. Garadkar, A. Gole, One pot synthesis of magnetite-silica nanocomposites: applications as tags, entrapment matrix and water purification, J. Mater. Chem. A 1 (2013) 20–26.
[176] H. Zhang, G.Y. Zhang, X. Bi, X.T. Chen, Surface modification of Li-rich layered Li (Li0.17Ni0.25Mn0.58)O_2 oxide with Li-Mn-PO_4 as the cathode for lithium-ion batteries, J. Mater. Chem. A 1 (2013) 5262–5268.
[177] J. Liu, Z.K. Sun, Y.H. Deng, Y. Zou, C.Y. Li, X.H. Guo, L.Q. Xiong, Y. Gao, F.Y. Li, D.Y. Zhao, Fabrication of magnetite hollow porous nanocrystal shells as a drug carrier for paclitaxel, Angew. Chem. Int. Ed. 48 (2009) 5875–5879.
[178] S.I. Srnova, B. Vlckova, Z. Bastl, T. Hasslett, Bismith metallic Ag Au microspheres prepared by the seed growth method: two dimensional assembly characterization by energy dispersive X-rays analysis, photoelectron spectroscopy, and surface enhanced Raman spectroscopy and proposed mechanism of growth, Langmuir 20 (2004) 3407–3415.
[179] D.H. Chen, Formation and characterization of Au-Ag bimetallic microspheres in water in oil microemulsions, J. Mater. Chem. C 12 (2002) 1557–1562.
[180] B. Binks, Particles as surfactants similarities and differences, Curr. Opin. Colloid Interface Sci. 7 (2002) 21–41.
[181] M.E. Leunissen, A. van Blaaderen, A. Hollingsworth, M.T. Sullivan, P. Chaikin, Electrostatics at the oil water interface, stability, and order in emulsions and colloids, Process Natural Academy Science USA 104 (2007) 258–2590.
[182] A. Stocco, E. Rio, B. Binks, D. Langevin, Aqueous foams stabilized solely by particles, Soft Matter 7 (2011) 1260–1267.
[183] C.D.H. Alarcon, S.A. Pennadam, Stimuli responsive polymers for biomedical applications, Chem. Soc. Rev. 34 (2005) 276.
[184] Y. Pardo, V. Gabai, R. Shipway, A.N. Bourenko, T. Willner, Gold nanoparticle/hydrogel composites with solvent-switchable electronic properties, Adv. Mater. 13 (2001) 1320–1323.
[185] F.Y. Pong, M. Lee, J.R. Bell, N.T. Flynn, Thermoresponsive poly(N-isopropylacrylamide) hydrogels containing gold nanostructures, Langmuir 22 (2006) 3851–3857.
[186] D. Dendukuri, P.S. Doyle, The synthesis and assembly of polymeric microparticles using microfluidics, Adv. Mater. 21 (2009) 4071–4086.
[187] Y.W. Jun, J.S. Choi, Shape control of semiconductor and metal oxide nanocrystals through non hydrolytic colloidal routes, Angew. Chem. Int. Ed. 45 (2006) 3414–3439.
[188] P.G. Degennes, Janus particle micro shuttle: 1D directional self-propulsion modulated by AC electrical field, Angew. Chem. Int. Ed. 31 (1992) 842–845.
[189] A. Walther, A.H.E. Muller, Janus particles, Soft Matter 4 (2008) 663–668.
[190] E. Duguet, A. Desert, A. Perro, S. Ravaine, Amorphous nanophotonics, Chem. Soc. Rev. 40 (2011) 941–960.
[191] H. Ma, L.F. Kakim, C.N. Bowman, R.H. Davis, Factors affecting membrane fouling reduction by surface modification and back pulsing, J. Membr. Sci. 189 (2001) 255–270.
[192] Z.K. Xu, J.L. Wang, L.Q. Shen, D.F. Meng, Y.Y. Xu, Microporous polypropylene hollow fiber membrane: part I. Surface modification by the graft polymerization of acrylic acid, J. Membr. Sci. 196 (2002) 221–229.
[193] C.F. Wang, N.T. Langer, Controlled structure and properties of thermoresponsive nanoparticle hydrogel composites, Adv. Mater. 16 (2004) 1074–1079.
[194] W.H. Binder, Supramolecular assembly of microspheres at liquid-liquid interfaces, Angew. Chem. Int. Ed. 44 (2005) 5172–5175.
[195] D.Y. Wang, H.W. Duan, H. Möhwald, The water/oil interface: the emerging horizon for self-assembly of microspheres, Soft Matter 1 (6) (2005) 412–416.
[196] J. Wang, D. Wang, N.S. Sobal, M. Giersig, M. Jiang, H. Mohwald, Stepwise directing of nanocrystals to self-assemble at water/oil interfaces, Angew. Chem. Int. Ed. 45 (2006) 7963–7966.
[197] J. Liu, Z.K. Sun, Y.H. Deng, Y. Zou, C.Y. Li, X.H. Guo, L.Q. Xiong, Y. Gao, F.Y. Li, D.Y. Zhao, Highly water dispersible biocompatible magnetite particles with low cytotoxicity stabilized by citrate groups, Angew. Chem. Int. Ed. 48 (2009) 5875–5879.
[198] F. Reincke, W.K. Kegel, H. Zhang, M. Nolte, D. Wang, D. Vanmaekelbergh, H. Mohwald, Understanding the self-assembly of charged microspheres at the water/oil interface, Phys. Chem. 8 (2006) 3828–3835.
[199] B.P. Binks, R. Murakami, S.P. Armes, S. Fujii, Temperature induced inversion of nanoparticle stabilized emulsions, Angew. Chem. Int. Ed. 44 (2005) 4873–4876.
[200] L. Ming, B. Shu, Y. Kun, S. Yan, Synthesis and characterization of magnetic polymer microspheres with a core-shell structure, China Particuology 5 (2007) 180–185.
[201] J. Li, W.D. He, X.L. Sun, J. Polym. Sci. A: preparation of poly(styrene-b-N-isopropylacrylamide) micelles surface-linked with gold nanoparticles and thermo-responsive ultraviolet–visible absorbance, Polym. Chem. 45 (2007) 5156–5163.
[202] Y.N. Zhou, J.J. Li, Z.H. Luo, Toward efficient water/oil separation material: effect of copolymer composition on pH-responsive wettability and separation performance, AICHE J. 62 (2016) 1758–1771.
[203] R.A. Vaia, J.F. Maguire, Polymer nanocomposites with prescribed mor-phology: going beyond nanoparticle-filled polymers, Chem. Mater. 19 (2007) 2736–2751.
[204] Y. Tian, B. Su, L. Jiang, Interfacial material system exhibiting superwettability, Adv. Mater. 26 (2014) 6872–6897.
[205] S. Wang, K. Liu, X. Yao, L. Jiang, Bioinspired surfaces with superwettability: new insight on theory, design, and applications, Chem Rev 115 (2015) 8230–8293.
[206] W. Zhang, L. Shi, R. Ma, Y. An, Y. Xu, K. Wu, Micellization of thermo- and pH-responsive triblock copolymer of poly(ethylene glycol)-b-poly(4-vinylpyridine)-poly(N-isopropylacrylamide), Macromolecules 38 (2005) 8850–8852.
[207] Z. Geng, S. Guan, Hm Jiang, Gao Lc, Z. Liu, L. Jiang, pH-Sensitive wettability induced by topological and chemical transition on the self assembled surface of block copolymer, Chin. J. Polym. Sci. 32 (2014) 92–97.
[208] Zhenkun Sun, Xinran Zhou, Wei Luo, Qin Yue, Yu Zhang, Xiaowei Cheng, Wei Li, Biao Kong, Yonghui Deng, Dongyuan Zhao, Interfacial engineering of magnetic particles with porous shells: towards magnetic core – porous shell microparticles, Nano Today 11 (2016) 464–482.
[209] M.A. Shannon, P.W. Bohn, M. Elimelech, J.G. Georgiadis, B.J. Marinas, A.M. Mayes, Science and technology for water purification in the coming decades, Nature 452 (7185) (2008) 301–310.
[210] J. Aurell, B.K. Gullett, Aerostat sampling of PCDD/PCDF emissions from the gulf oil spill in situ burns, Environ. Sci. Technol. 44 (24) (2010) 9431–9437.
[211] L.P. Xu, X.W. Wu, J.X. Meng, J.T. Peng, Y.Q. Wen, X.J. Zhang, S.T. Wang, Papilla-like magnetic particles with hierarchical structure for oil removal from water, Chem. Commun. 49 (78) (2013) 8752–8754.
[212] E. Barry, J.A. Libera, A.U. Mane, J.R. Avila, D. DeVitis, K. Van Dyke, J.W. Elam, S.B. Darling, Mitigating oil spills in the water column, Environ. Sci. Water Res. Technol. 4 (1) (2018) 40–47.
[213] Q. Zhu, F. Tao, Q. Pan, Fast and selective removal of oils from water surface via highly hydrophobic core-shell Fe_2O_3@C nanoparticles under magnetic field, ACS Appl. Mater. Interfaces 2 (11) (2010) 3141–3146.
[214] P. Calcagnile, D. Fragouli, I.S. Bayer, G.C. Anyfantis, L. Martiradonna, P.D. Cozzoli, R. Cingolani, A. Athanassiou, Magnetically driven floating foams for the removal of oil contaminants from water, ACS Nano 6 (6) (2012) 5413–5419.
[215] G. Zhao, X. Huang, Z. Tang, Q. Huang, F. Niu, X. Wang, Polymer-based nanocomposites for heavy metal ions removal from aqueous solution: a review, Polym. Chem. 9 (2018) 3562–3582.

[216] J. Li, X. Wang, G. Zhao, C. Chen, Z. Chai, A. Alsaedi, T. Hayat, X. Wang, Metal—organic framework-based materials: superior adsorbents for the capture of toxic and radioactive metal ions, Chem. Soc. Rev. 47 (2018) 2322–2356.
[217] X.-L. Wu, L. Wang, C.-L. Chen, A.-W. Xu, X.-K. Wang, Water-dispersible magnetite-graphene-LDHs composites for efficient arsenate removal, J. Mater. Chem. 21 (2011) 17353–17359.
[218] P. Gu, S. Zhang, X. Li, X. Wang, T. Wen, R. Jehan, A. Alsaedi, T. Hayat, X. Wang, Recent advances in layered double hydroxidebased nanomaterials for the removal of radionuclides from aqueous solution, Environ. Pollut. 240 (2018) 493–505.
[219] Soubantika Palchoudhury, Jamie R. Lead, A facile and cost-effective method for separation of oil—water mixtures using polymer-coated iron oxide nanoparticles, Environ. Sci. Technol. 48 (2014) 14558–14563.
[220] Guoqiang Liu Meirong Cai, Xiaolong Wang, Feng Zhou, Weimin Liu, Core—shell—corona-structured polyelectrolyte brushes-grafting magnetic nanoparticles for water harvesting, ACS Appl. Mater. Interfaces 6 (2014), 11625—11632. .
[221] Alexander V. Dudchenko, Julianne Rolf, Lucy Shi, Liana Olivas, Wenyan Duan, David Jassby, Coupling underwater superoleophobic membranes with magnetic Pickering emulsions for fouling-free separation of crude oil/water mixtures: an experimental and theoretical study, 9 (10) (2015) 9930–9941.
[222] Yu Zhou Ning Zhang, Xiang Zhou Yubing Hu, Gazi Hao Xiaodong Li, Wei Jiang, Design of recyclable superhydrophobic PU@Fe3O4@PS sponge for removing oily contaminants from water, Ind. Eng. Chem. Res. 58 (2019) 3249–3257.
[223] Liuhua Yu, Gazi Hao, Qianqian Liang, Wei Jiang, Fabrication of magnetic porous silica submicroparticles for oil removal from water, Ind. Eng. Chem. Res. 54 (2015) 9440–9449.
[224] Bo Zhang, Runtao Hu, Dejun Sun, Tao Wu, Yujiang Li, Fabrication of magnetite-graphene oxide/MgAl-layered double hydroxide composites for efficient removal of emulsified oils from various oil-in-water emulsions, J. Chem. Eng. Data 63 (2018) 4689–4702.
[225] Jianrui Zhang Yiming Li, Mutai Bao Xiaolong Yang, Zhining Wang, Facile fabrication of cyclodextrin-modified magnetic particles for effective demulsification from various types of emulsions, Environ. Sci. Technol. 50 (2016) 8809–8816.
[226] Ning Zhang, Wei Jiang, Tianhe Wang, Junjun Gu, Suting Zhong, Shuai Zhou, Tan Xie, Jiajun Fu, Facile preparation of magnetic poly(styrene-divinylbenzene) foam and its application as an oil absorbent, Ind. Eng. Chem. Res. 54 (2015) 11033–11039.
[227] Yu Liuhua, Gazi Hao, Gu Junjun, Shuai Zhou, Ning Zhang, Wei Jiang, Fe_3O_4/PS magneticnanoparticles: synthesis, characterization and their application assorbents of oil from wastewater, J. Magn. Magn. Mater. 394 (2015) 14–21.
[228] Shuai Zhou, Wei Jiang, Tianhe Wang, Lu Yue, Highly hydrophobic, compressible, and magnetic polystyrene/Fe_3O_4/graphene aerogel composite for oil—water separation, Ind. Eng. Chem. Res. 54 (2015) 5460–5467.
[229] Lei Wu, Lingxiao Li, Bucheng Li, Junping Zhang, Aiqin Wang, Magnetic, durable, and superhydrophobic polyurethane@Fe_3O_4@SiO_2@Fluoropolymer sponges for selective oil absorption and oil/water separation, ACS Appl. Mater. Interfaces 7 (2015) 4936–4946.
[230] Xiao He, Chen Liang, Qingxia Liu, Zhenghe Xu, Magnetically responsive Janus nanoparticles synthesized using cellulosic materials for enhanced phase separation in oily wastewaters and water-in crude oil emulsions, Chem. Eng. J. 378 (2019), 122045. .
[231] Xiaoyang Wang, Yao Lu, Claire J. Carmalt, Ivan P. Parkin, Xia Zhang, Multifunctional porous and magnetic silicone with high elasticity, durability, and oil—water separation properties, Langmuir 34 (2018), 13305—13311. .
[232] Xiaohui Mao, Lu Gong, Lei Xie, Hui Qian, Xiaogang Wang, Hongbo Zeng, Novel Fe_3O_4 based superhydrophilic core-shell microspheres for breaking asphaltenes-stabilized water-in-oil emulsion, Chem. Eng. J. 358 (2019) 869–877.
[233] Seyyedali Mirshahghassemi, Jamie R. Lead, Oil recovery from water under environmentally relevant conditions using magnetic nanoparticles, Environ. Sci. Technol. 49 (2015) 11729–11736.
[234] Junxia Peng, Qingxia Liu, Zhenghe Xu, Jacob Masliyah, Novel magneticd for water removal from diluted. Bitumen emulsion, Energy Fuel 26 (2012) 2705–2710.
[235] Jiatu Li, Mizuki Tenjimbayashi, Nicole S. Zacharia, Seimei Shiratori, One-step dipping fabrication of Fe3O4/PVDF-HFP composite 3D porous sponge for magnetically controllable oil—water separation, ACS Sustain. Chem. Eng. 6 (2018) 10706–10713.
[236] Zeng-Tian Li, Hao-Tong Wu, Wan-Yi Chen, Fu-An He, De-Hao Li, Preparation of magnetic superhydrophobic melamine sponges for effective oil-water separation, Sep. Purif. Technol. 212 (2019) 40–50.
[239] Ni Wang, Ziwei Deng, Synthesis of magnetic, durable and superhydrophobic carbon sponges for oil/water separation, Mater. Res. Bull. 115 (2019) 19–26.
[240] Shuqiang Li, Naixu Li, Shanbo Yang, Fangyuan Liu, Jiancheng Zhou, The synthesis of a novel magnetic demulsifier and its application for the demulsification of oilcharged industrial wastewaters, J. Mater. Chem. A 2 (2014) 94.
[241] Du Ran, Qiuchen Zhao, Pan Li, Huaying Ren, Xin Gao, Jin Zhang, Ultrathermostable, magnetic-driven, and superhydrophobic quartz fibers for water remediation, ACS Appl. Mater. Interfaces 8 (2016) 1025–1032.
[242] Ning Chen, P. Qinmin, Versatile fabrication of ultralight magnetic foams and application for oil-water separation, 7 (8) (2013) 6875–6883.
[243] K.Y. Tan, T.L. Hughes, M. Nagl, W.T. Huck, Nonfouling capture-release substrates based on polymer brushes for separation of water-dispersed oil droplets, ACS Appl. Mater. Interfaces 4 (2012) 6403–6409.
[244] M. Kobayashi, Y. Terayama, H. Yamaguchi, M. Terada, D. Murakami, K. Ishihara, A. Takahara, Wettability and antifouling behavior on the surfaces of superhydrophilic polymer brushes, Langmuir 28 (2012) 7212–7222.
[245] A. Farrukh, A. Akram, A. Ghaffar, S. Hanif, A. Hamid, H. Duran, B. Yameen, Design of polymer-brush-grafted magnetic nanoparticles for highly efficient water remediation, ACS Appl. Mater. Interfaces 5 (2013) 3784–3793.
[246] J. Yan, B. Li, B. Yu, W.T. Huck, W. Liu, F. Zhou, Controlled polymer-brush growth from microliter volumes using sacrificial- anode atom-transfer radical polymerization, Angew. Chem. Int. Ed. 52 (2013) 9125–9129.
[247] B. Li, B. Yu, W.T. Huck, F. Zhou, W. Liu, Electrochemically induced surface-initiated atom-transfer radical polymerization, Angew. Chem. Int. Ed. 51 (2012) 5092–5095.
[248] J. Zheng, Y. Dong, W. Wang, Y. Ma, J. Hu, X. Chen, X. Chen, In situ loading of gold nanoparticles on Fe3O4@SiO2 magnetic nanocomposites and their high catalytic activity, Nanoscale 5 (2013) 4894–4901.
[250] A.H. Lu, E.L. Salabas, F. Schuth, Magnetic nanoparticles: synthesis, protection, functionalization, and application, Angew. Chem. Int. Ed. 46 (2007) 1222–1244.
[251] M. Panagiotopoulou, S. Beyazit, S. Nestora, K. Haupt, B.T.S. Bui, Initiator-free synthesis of molecularly imprinted polymers by polymerization of self-initiated monomers, Polymer 66 (2015) 43–51.
[252] P. Xiao, J.C. Gu, J. He, S. Wang, J.W. Zhang, Y.J. Huang, S.W. Kuo, T. Chen, Integration of a patterned conductive carbon nanotube thin film with an insulating hydrophobic polymer carpet into robust 2D Janus hybrid flexible electronics, J. Mater. Chem. C 4 (41) (2016) 9750–9755.
[253] P. Xiao, C.J. Wan, J.C. Gu, Z.Z. Liu, Y.H. Men, Y.J. Huang, J.W. Zhang, L.Q. Zhu, T. Chen, 2D Janus hybrid materials of polymer-grafted carbon nanotube/graphene oxide thin film as flexible, miniature electric carpet, Adv. Funct. Mater. 25 (16) (2015) 2428–2435.