Fuel 206 (2017) 453–466

Contents lists available at ScienceDirect

Fuel

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

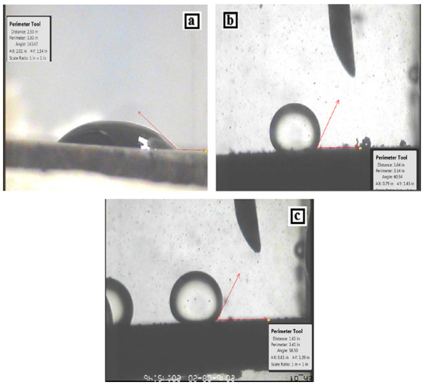
Full Length Article

Facile and economical preparation method of nanoporous graphene/silica nanohybrid and evaluation of its Pickering emulsion properties for Chemical Enhanced oil Recovery (C-EOR)

M. AfzaliTabar [a], M. Alaei [b,*], M. Bazmi [b], R. Ranjineh Khojasteh [a], M. Koolivand-Salooki [c], F. Motiee [a], A.M. Rashidi [b]

[a] Department of Chemistry, Islamic Azad University Branch of Tehran North, Tehran, Iran
[b] Nanotechnology Research Center, Research Institute of Petroleum Industry (RIPI), Tehran, Iran
[c] Gas Research Division, Research Institute of Petroleum Industry (RIPI), Tehran, Iran

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 12 January 2017
Received in revised form 8 April 2017
Accepted 30 May 2017

Keywords:
Chemical enhanced oil recovery
Nanohybrid
Pickering emulsion
Nanoporous graphene
Multi walled carbon nanotubes
Polymer flooding technique

ABSTRACT

In this research, we have proposed a very simple and economical preparation method for nanoporous graphene/silica nanohybrid (sol–gel method) that the related Pickering emulsion will be suitable for Chemical Enhanced Oil Recovery (C-EOR). This preparation method is preferred to the similar previous researches. For evaluation of the mentioned Pickering emulsion properties, we have prepared other carbon structures (MWCNT and graphite)/SiO_2 nanohybrids with different weight percent. The as-prepared nanomaterials were characterized with X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Thermal Gravimetric Analysis (TGA).

The nanohybrids Pickering emulsions were prepared with n-Octane as oil model, suitable anionic surfactant (such as SDBS) and 2-Propanol as alcoholic co-surfactant at pH = 7 in ambient temperature and with distilled water. The mentioned Pickering emulsions stability was controlled for one month. Emulsion phase morphology was investigated with optical microscopic image. Evaluation results demonstrated that the best samples are MWCNT/SiO_2 and nanoporous graphene/SiO_2 nanohybrids. Stability of the selected nanohybrids was investigated by alteration of salinity, pH and temperature and results showed that the related Pickering emulsions of the selected nanohybrids have very good stability at 1% salinity, ambient and several oil reservoir temperatures (25 °C, 90 °C, 105 °C and 120 °C) and neutral and alkaline (7,10) pH that is suitable for the oil reservoirs conditions but contact angle measurement

---

[*] Corresponding author.
E-mail address: alaiem@ripi.ir (M. Alaei).

http://dx.doi.org/10.1016/j.fuel.2017.05.102

results showed that the nanoporous graphene/SiO_2 nanohybrid is more effective for improvement of the stone reservoir wettability alteration from oil-wet to water-wet in comparison to the other samples. Interfacial tension evaluations indicate that the maximum amount is related to the injection of water and the minimum amount is related to the injection of nanoporous graphene/SiO_2 nanohybrid nanofluid. This result indicates the nano porous graphene/SiO_2 nanohybrid can better reduce the interfacial tension in comparison to the other samples. Our results demonstrated that the nanoporous graphene/SiO_2 nanohybrids Pickering emulsion has superior properties to the MWCNT/SiO_2 nanohybrids Pickering emulsion (that we presented in our previous research) for Chemical Enhanced Oil Recovery (C-EOR) and the nanoporous graphene/SiO_2 nanohybrid can improve the rheological behaviour of polymer suspensions that are suitable for polymer flooding technique.

1. Introduction

Because of increasing demand for oil particularly in the developed and developing countries, well productivity improvement is very important. Also the discovery of new oil fields is very limited [1]. Two thirds of the original oil in place (OOIP) in a reservoir is not produced and needs for recovery by suitable EOR methods is obvious. The entrapped oil can be recovered if the capillary forces, whose strength is set by the oil/water interfacial tension (IFT) are reduced by three to four orders of magnitude and viscosity of the displacing fluids increases [2].

Most of the oil reservoirs are hardly having uniform porosities, thus when water or other fluids are injected at high pressure condition, they generally follow the path of the least resistance formation section and cause early breakthrough of injected fluids. This causes the trapped oil by-passed in the lower permeability zones. Chemical flooding is one of the best EOR processes that can be used to recover up to an additional 35% of OOIP and is one of the major EOR techniques especially for reservoirs where thermal methods are not feasible. Recently chemical flooding in different modes like injection of polymer, polymer/alkaline, surfactant/polymer, alkaline/surfactant/polymer (ASP) and microemulsion are getting more importance because of significant potentiality [1,3–7]. EOR by microemulsion flooding has become more attractive in recent years in order to its high level of extraction efficiency [8–11]. Microemulsion flooding is preferred over alkali, surfactant or polymer flooding due to unique physicochemical properties like production of ultra-low IFT, moderate viscosity, good water solubilisation capacity and nano sized droplets. Another important property of microemulsion is its droplet size. In particular, the size distribution of microemulsion gives essential information for reasonable understanding of the governing mechanism of the both stability and porous media diffusion. Several mechanisms such reduction of IFT, emulsification of oil and water, solubilisation of interfacial films, wettability reversal, viscosity improvement, etc., are responsible for the improved oil recovery [1]. It has been known that emulsions could remain stable by adding suitable surfactants for a long time. A new method that is called Pickering emulsion that stabilized by solid particles instead of organic surfactants is used in recent years [12]. Comparison between Pickering emulsions which are stabilized by particles and classical emulsions which are stabilized by surfactants, show that Pickering emulsions have increased stabilities [13,14]. In general, hydrophobic and hydrophilic properties of particles will determine the type of emulsions, so hydrophilic particles tend to stabilize the oil- in-water (o/w) emulsions, while the water- in- oil (w/o) are better stabilized by the hydrophobic particles [15–19]. Pickering emulsion system was recently studied by many researchers for many different targets especially in enhanced oil recovery. Alaei and co-workers, prepared multi walled carbon nanotube/silica nanohybrids to investigate the effects of nanofluid on the wettability of carbonate and sandstone rocks [19]. Ajay Mandal and co-workers, reported the suspension of silica nanoparticle behaviour in aqueous polyacrylamide solution for application in enhanced oil recovery [20]. Resasco and Shen reported the preparation of carbon nanotube - silica nanohybrids to form oil- in -water and water-in-oil emulsions with different volume fraction of emulsion [21]. Ames et al. prepared organic- inorganic hybrid microspheres by nanoparticles of silica as Pickering emulsifier [22–23]. To prevent the aggregation of nanoparticles, they are often used with different supports such as carbon nanotube [19,23] and graphene oxide (GO) are often used [18]. It has been found that GO could be a fine support [25–29] for metal nanoparticles such as silver [30], gold [31], platinum [32], palladium [33]. Graphene is a monolayer of carbon atoms that arrange in hexagonal lattice [25–26]. It has excellent optical, mechanical and electronic properties [27–28]. If natural graphite oxidized, graphene oxide is formed [34–35]. The oxidation process causes GO sheets disperse in water and other polar solvents because of the several oxidation groups formation such as carboxyl, epoxy and hydroxyl at the edges [36]. Therefore, GO has an amphiphile surface with hydrophilic edges and hydrophobic plane [37]. In addition, GO has many applications such as catalytic supports for chemical reactions [38–39], adsorption [40–41] and separation of pollutants [42].

There are several methods for the preparation of carbon structures nanohybrids with Silica nanoparticle such as Chemical Vapour Deposition (CVD), solvothermal, hydrothermal, Ball Milling, electro deposition method, sol–gel, sonochemical and co-precipitation method. Among of these mentioned preparation procedures, sol–gel is the best method because the required chemical compounds are economical and simple, reaction take places at low temperature so process steps are very safe, process produce high purity products, simplicity of the required equipments and feasibility for up-scaling of the method.

As reported in the previous research graphene/silica nanohybrid was synthesized through a chemical vapour deposition method on silica aerogel in the presence of hydrogen and acetylene at atmospheric pressure and 600 °C [43]. This synthesis method take place at high temperature, dangerous gas like hydrogen and acetylene are necessary for the reaction and it needs silica aerogel which its synthesis method is time-consuming and also requires expensive materials [43]. In this research, facile and economical preparation method of nanoporous graphene/silica nanohybrid was proposed.

In fact, this is a low temperature sol–gel method with very simple and facile steps without using any dangerous and harmful materials. Besides this synthesis method dose not produce environment pollutant and it is the economical method because of simplicity of process steps, conventional and cheep equipments and possibility for using of the all required chemical materials in commercial grades (such as commercial sodium silicate solution as silica source).

For evaluation of the mentioned Pickering emulsion in comparison to the similar nanohybrids, we have prepared different carbon structures nanohybrids with SiO_2 nanoparticles with different weight percent. The as-prepared nanomaterials were characterized with X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Thermal Gravimetric Analysis (TGA).

The nanohybrids Pickering emulsions were prepared with n-Octane as oil model, suitable anionic surfactant (such as SDBS) and 2-Propanol as alcoholic co-surfactant at pH = 7 in ambient temperature with distilled water. The mentioned Pickering emulsions stability was controlled for one month. Optical microscopic image was used for emulsion phase morphology investigation. Results demonstrated that the best samples are MWCNT/SiO_2 and nanoporous graphene/SiO_2 nanohybrids. The selected nanohybrids stability was investigated by alteration of salinity, pH and temperature and results showed that the related Pickering emulsions of the selected nanohybrids have very good stability at 1% of salinity and ambient temperature of 25 °C and also several oil reservoir temperatures (90 °C, 105 °C and 120 °C) with neutral and alkaline pH (7,10) that is suitable for the oil reservoirs conditions. But contact angle measurement results showed that the nanoporous graphene/SiO_2 nanohybrid is more effective for improvement of the reservoir outcrop wettability alteration from oil-wet to water-wet in comparison to the other samples. Interfacial tension evaluations indicate that the maximum amount is related to the injection of water and the minimum amount is related to the injection of nanoporous graphene/SiO_2 nanohybrid nanofluid. This result indicates the nanoporous graphene/SiO_2 nanohybrid can better reduce the interfacial tension in comparison to the other samples. Our results demonstrated that the nanoporous graphene/SiO_2 nanohybrids Pickering emulsion has superior properties to the MWCNT/SiO_2 nanohybrids Pickering emulsion (that we presented in our previous research [48]) for C-EOR and the nano porous graphene/SiO_2 nanohybrid can improve the rheological behaviour of polymer suspensions that are suitable for polymer flooding technique.

2. Materials and methods

Nanoporous graphene and MWCNT were supplied by nanotechnology research center of Research Institute of Petroleum Industry (RIPI) that were prepared with Chemical Vapour Deposition (CVD) method by different conditions. Graphite, sodium silicate (SiO_2/Na_2O = 3.35), sodium dodecyl benzene sulfonic acid (SDBS), 2-Propanol and n-Octane were used as received from Merck chemical company without any further purification.

The prepared nanomaterials were characterized by Scanning Electron Microscope (SEM) by using a Holland Phillips XL30 microscope. The XRD patterns of the all samples were recorded in ambient air using a Holland Philips X-ray powder diffraction (Cu Ka, k = 1.5406 Å), at scanning speed of 2°/min from 20° to 80°. Transmission Electron Microscopy (TEM) images were prepared with a Philips EM 208 FEG instrument operating at 90 kV. Optical microscopic images were prepared with Quantimet-570 microscope. Rheological studies were performed using a Fann 35 Rheometer. Nanohybrids were prepared by addition of carbon compound mean while the preparation of Silica nanoparticles by sol–gel method with different weight percents.

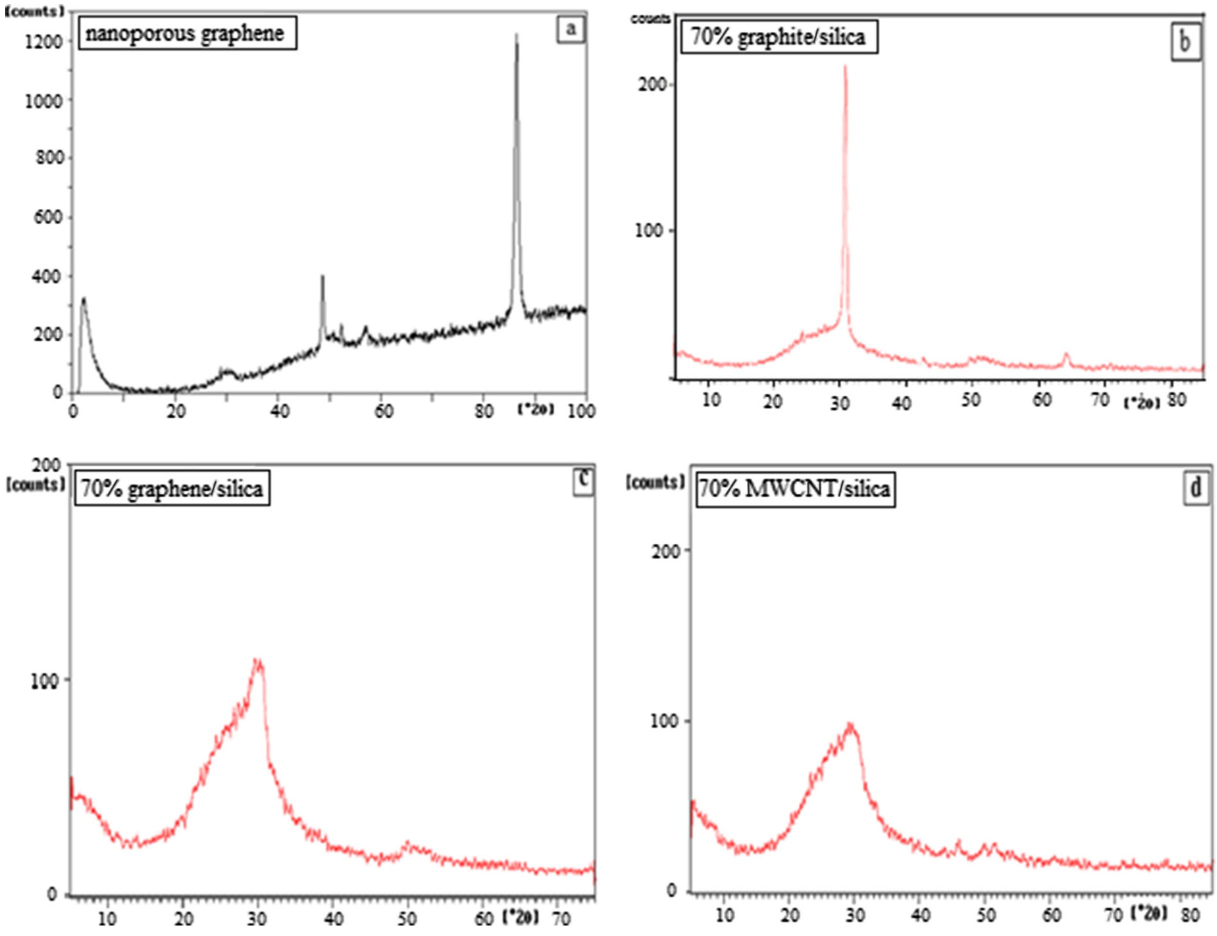


Fig. 1. XRD patterns of (a) nanoporous graphene (b) 70% graphite/SiO_2 nanohybrid (dc) 70% graphene/SiO_2 nanohybrid and (d) 70% MWCNT/SiO_2 nanohybrid.

3. Experimental procedures

3.1. Functionalization of carbon compounds

Nanoporous graphene and MWCNT that were received from Research Institute of Petroleum Industry (RIPI) and graphite (Merck company product) have been acid treated with concentrated HNO_3. 0.66 wt% of Carbon compounds is added to a mixture of 52.98 wt% distilled water and 46.36 wt% Nitric acid and let it refluxed for 10 h. After filtration and neutralization with distilled water, sample dried in oven at 60 °C.

3.2. Synthesis of carbon structures/Silica nanohybrid

9.09 wt% of commercial sodium silicate solution was dissolved in 90.90 wt% of HCl 2.5%. Suitable amount of the functionalized Carbon structure for preparation of 70, 50 and 10 wt% nanohybrids was dispersed in the solution. After about 5 h of mixing, solution washed with distilled water and dried in oven at 60 °C.

3.3. Preparation of Pickering emulsions

0.09 wt% of nanohybrid was dissolved in 88.97 wt% of distilled water and then sonicated for 10 min in ultrasonic bath. 0.27 wt% of SDBS, 5.34 wt% of 2-Propanol and 5.34 wt% of n-decane as Oil model added to the solution, respectively. Then the procedure was continued by sonicating of the prepared samples for 10 min again. The Pickering emulsions stability of these nanohybrids were investigated for one month at pH = 7 and ambient temperature.

3.4. Surface pH

The surface acidity can be characterized by pH measurement of an adsorbent sample suspension [44]. Then 1.96 wt% of the sample was added to 98.04 wt% of distilled water, and the suspension was

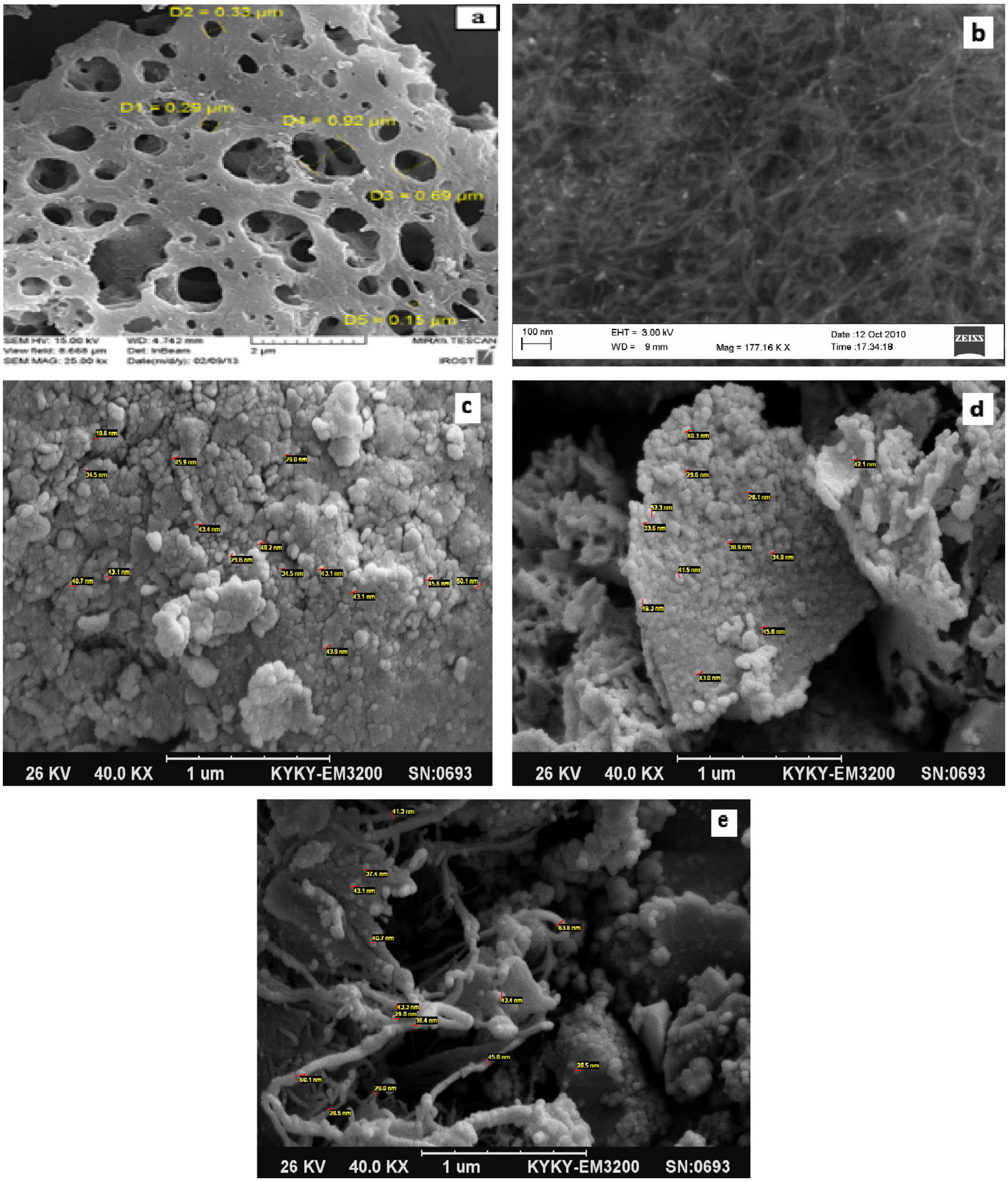


Fig. 2. SEM images of (a) nanoporous graphene (b) MWCNT (c) 70% graphite/SiO_2 nanohybrid (d) 70% graphene/SiO_2 and (e) 70% MWCNT/SiO_2 nanohybrid.

shaken overnight till the sample reach to equilibrium and then the suspensions pH was measured.

4. Result and discussion

With respect to the emulsion stability, the selection of the as-prepared nanohybrids for XRD, SEM and TGA analysis was performed. XRD patterns of nanoporous graphene, 70% graphite/SiO_2 nanohybrid, 70% nanoporous graphene/SiO_2 nanohybrid and 70% MWCNT/SiO_2 nanohybrid were shown in Fig. 1a–d, respectively. The characteristic peak of nanoporous graphene is about 29.08° that is observed in Fig. 1a and indicates the existence of nanoporous graphene with single or a few layers [45,46]. 70% graphite/SiO_2 has 2 main peaks in 30° and 64° that belongs to the graphite (Fig. 1b). Pure graphite indicates a very strong and sharp peak at 25.97° [46] that is shifted to 30° because of the silica nanoparticles existence with amorphous structure [19]. As can be seen in Fig. 1c–d, the amorphous silica nanoparticles structure [19] is dominant to graphene and MWCNT structures, therefore the related nanohybrids have amorphous structures.

The morphologies of the as-prepared nanohybrids were investigated by SEM images. Fig. 2 demonstrates the SEM images of nanoporous graphene, (Multi-Walled Carbon Nanotube) MWCNT, 70% graphite/SiO_2 nanohybrid, 70% graphene/SiO_2 nanohybrid and 70% MWCNT/SiO_2 nanohybrid. The layer and nanoporous structure of the graphene sample can be observed in Fig. 2a. Also in Fig. 2b, the tubular structure of (Multi-Walled Carbon Nanotube) MWCNT was presented. In Fig. 2c–e, the silica nanoparticles with spherical morphology that were uniformly attached to the related Carbon structure could be observed. Fig. 3 shows Transmission Electron Microscopy (TEM) images of the graphene and (Multi-Walled Carbon Nanotube) MWCNT morphologies in more precision. The layer and tubular structure of the graphene and (Multi-Walled Carbon Nanotube) MWCNT can be seen in Fig. 3 respectively that is confirmed the results of the related SEM images.

Thermal Gravimeteric analysis (TGA) results of 70% graphene/SiO_2 nanohybrid, 70% graphite/SiO_2 nanohybrid and 70% MWCNT/SiO_2 nanohybrid in nitrogen atmosphere concurrently warmed by temperature increasing rate of 0.1 °C/min are presented in Fig. 4. As can be seen, H_2O molecules were escaped from the samples at 100 °C. Nanoporous graphene has the high thermal stability [46] and therefore it has been degraded at about 600 °C, but graphite and MWCNT were degraded at about 260–270 °C. SiO_2 nanoparticles remain stable even at 800 °C because of high thermal stability.

Comparison between emulsion stability of graphite/Silica nanohybrids was shown in Fig. 5a. As can be seen, 70% graphite/silica nanohybrid emulsion has the lowest precipitation in comparison to the others. Comparison between emulsion stability of graphene/Silica nanohybrids was shown in Fig. 5b. The Fig. 5b illustrates, 70% nanoporous graphene/SiO_2 emulsion has lower precipitation in comparison to the others. Comparison between emulsion stability of MWCNT/Silica nanohybrids was shown in Fig. 5c. 70% MWCNT/SiO_2 nanohybrid emulsion has the lowest precipitation in comparison with the others. Therefore, Pickering emulsions of 70% graphite/Silica nanohybrid), 70% graphene/SiO_2 nanohybrids and 70% MWCNT/SiO_2 nanohybrid have the best stability in comparison to the other samples.

Optical microscopic images of the nanohybrids Pickering emulsions were shown in Fig. 6. According to the suitable optical microscopic images of such Pickering emulsions that can be used for C-EOR (reported by Professor Resasco et al. [21,24], the images in Fig. 6 were investigated. Suitable Pickering emulsion has homogenous dispersion of emulsion droplets with good compact that the solid particles of nanohybrids were surrounded them. By considering of the evaluation of emulsion stability (presented in Fig. 5), 70% graphite/SiO_2 nanohybrid has the best image in comparison with the other images that were depicted in Fig. 6a. In Fig. 6b, 70% nanoporous graphene/SiO_2 nanohybrid emulsions and in Fig. 6c, 70% MWCNT/SiO_2 nanohybrid emulsion were selected. Considering the optical microscopic images of the mentioned nanohybrid emulsions, it can be observed obviously that the 70% nanoporous graphene/SiO_2 nanohybrid emulsion and 70% MWCNT/SiO_2 nanohybrid emulsion have very uniform emulsion droplet size and dispersion and each of droplets were surrounded very well with solid particles of the related nanohybrid [47]. As can be seen 70% MWCNT/SiO_2 nanohybrid emulsion droplets are more compacted in comparison with the others.

Similar to the researches of Daniel Resasco and his co-workers [21], stability of the selected nanohybrids (70% graphene/SiO_2 nanohybrids and 70% MWCNT/SiO_2 nanohybrid were investigated by alteration of salinity, pH and temperature similar to the oil reservoirs conditions. Fig. 7 shows the stability evaluation of (a) 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions (b) 70% MWCNT/SiO_2 nanohybrid emulsion at different salinity of 0.1%, 1% and 10% (wt%) respectively. As Fig. 7 illustrates, 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions only stable

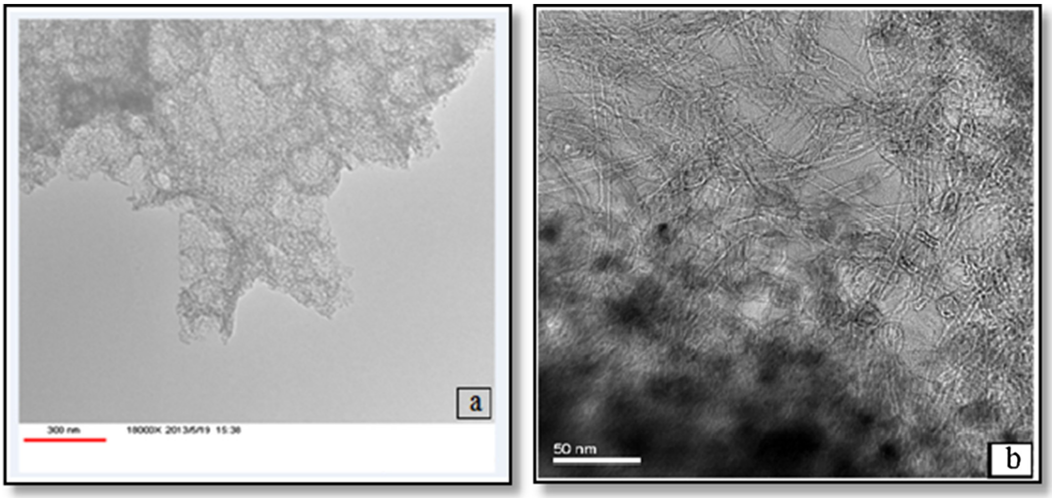


Fig. 3. TEM images of (a) nanoporous graphene and (b) MWCNT.

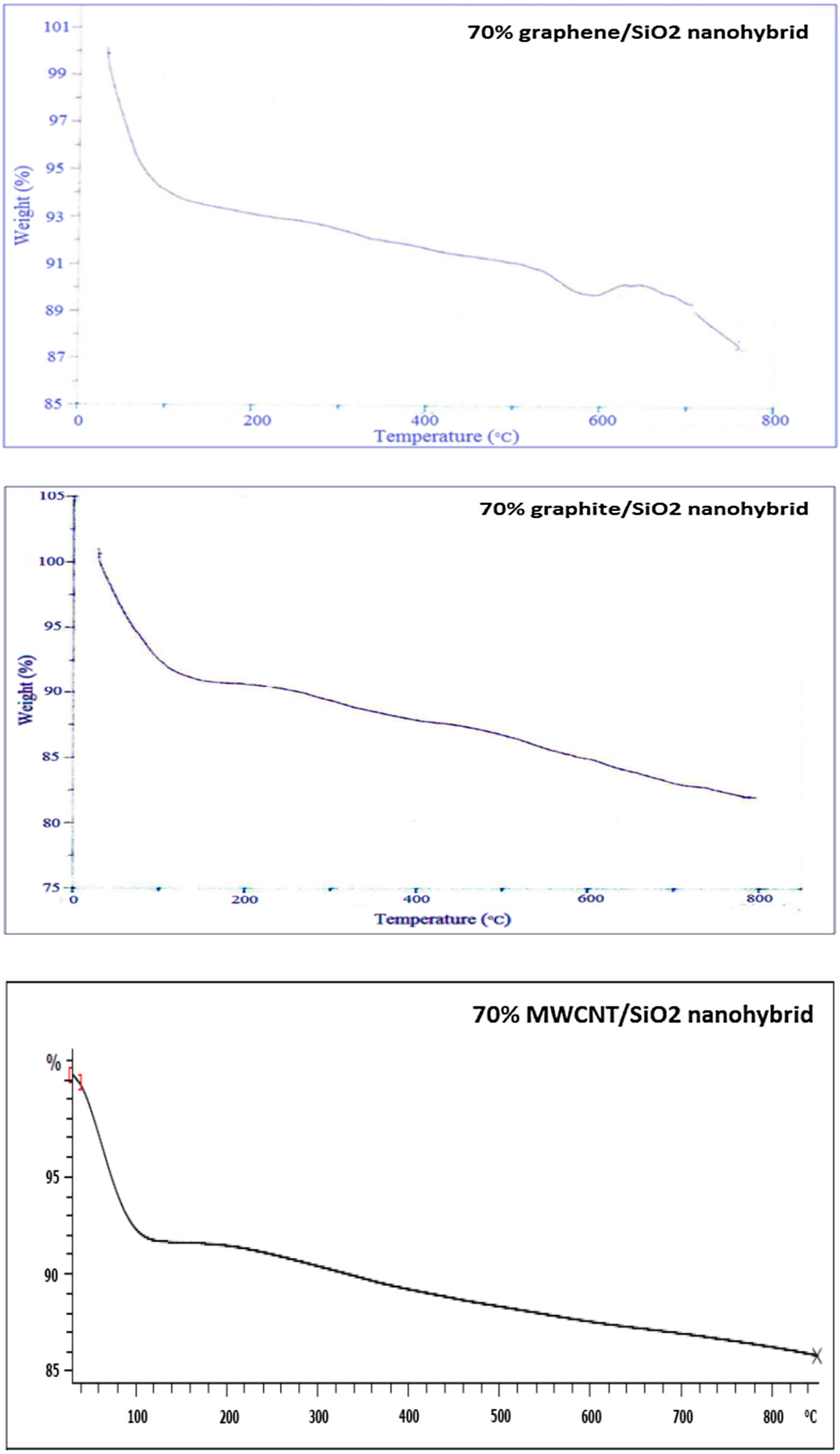


Fig. 4. Thermal Gravimetery Analysis (TGA) results of 70% graphene/SiO_2 nanohybrid, 70% graphite/SiO_2 nanohybrid and 70% MWCNT/SiO_2 nanohybrid.

at 1% of salinity but 70% MWCNT/SiO_2 nanohybrid emulsions are homogenous without any precipitation at 0.1%, 1% (wt%) of salinity. Therefore, the stability of 70% MWCNT/SiO_2 nanohybrid emulsion in various salinities is superior to the other specimens. Fig. 8 demonstrates the stability evaluation of (a) 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions (b) 70% MWCNT/SiO_2 nanohybrid emulsion at different pH (acidic (3) and alkaline (10)). This figure demonstrates that all of the Pickering emulsions have very good stability in alkaline environment (pH = 10) in comparison with the acidic media. Fig. 9 depicts the stability evaluation of (a) 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions (b) 70% MWCNT/SiO_2 nanohybrid emulsion at different oil

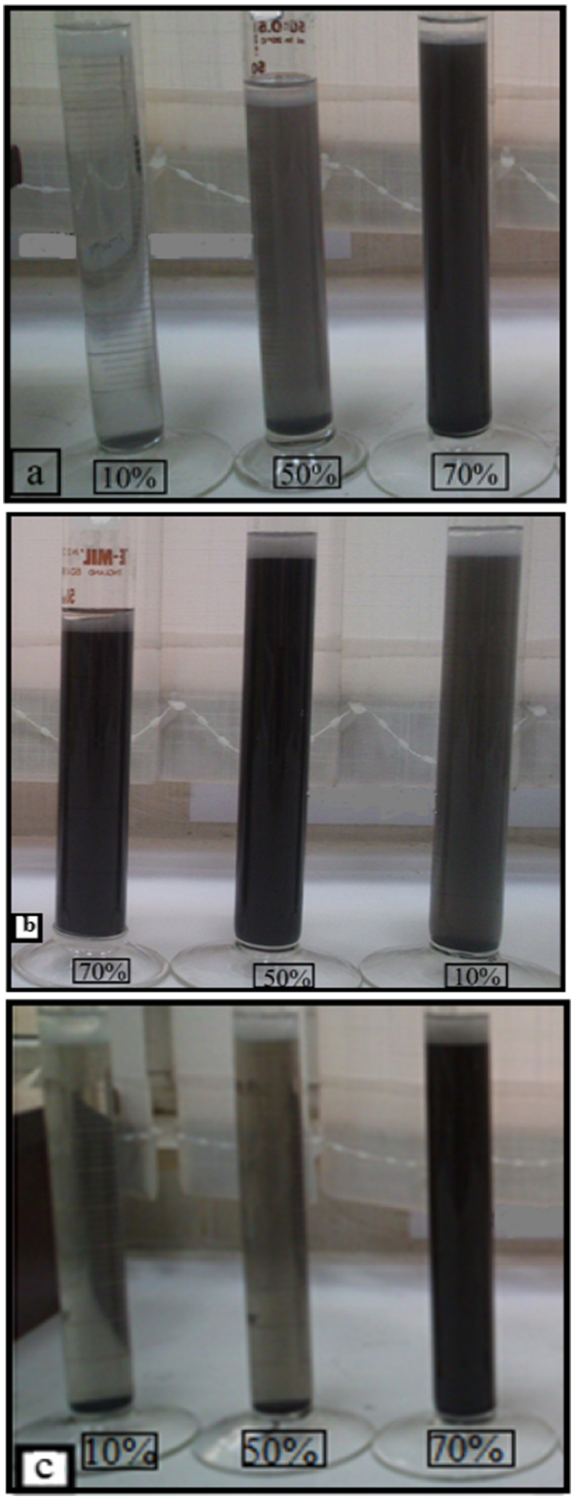


Fig. 5. Evaluation of the nanohybrids Pickering emulsion stability for one month (images related to (a) graphite/SiO_2 nanohybrid Pickering emulsions (b) nanoporous graphene/SiO_2 Pickering emulsions (c) MWCNT /SiO_2 nanohybrid Pickering emulsions.

reservoir temperatures such as 90 °C, 105 °C and 120 °C. It can be seen that all of the desired emulsions have good stability at ambient temperature (25 °C) and also at several oil reservoir temperatures (90 °C, 105 °C and 120 °C).

Fig. 10 shows the nanofluid contact angle measurement of 70% nanoporous graphene/SiO_2 nanohybrids and 70% MWCNT/SiO_2 nanohybrid. For measuring contact angle, the chamber is full of kerosene and water droplet or nano fluid droplet is injected by a syringe. In this condition, a contact angle below and over 90°, represents more hydrophilic and more hydrophobic samples, respectively. In this experiment just transparent oils could be selected for the contact angle measurements. Crude oil is dark and cannot be used in this experiment. The kerosene is applied as an oil model which is transparent and has a suitable hydrocarbon chain length with similar properties to the crude oil. According to the As Fig. 10 depicted, the contact angles of (a) water droplet and reservoir outcrop (b) water droplet and reservoir outcropping rock with a layer of MWCNT/SiO_2 nanohybrid (c) water droplet and reservoir outcrop with a layer of 70% nanoporous graphene/SiO_2 nanohybrid are 143.47, 60.54 and 58.50, respectively. Fig. 10 depicted, the 70% nanoporous graphene/SiO_2 nanohybrid has the least contact angle value in comparison with the other samples and it represents more hydrophilicity and so, alter the wettability of carbonate reservoir rock better from oil-wet to water-wet. Therefore, 70% nanoporous graphene/SiO_2 nanohybrid is more effective for the wettability alteration of reservoir rock from oil-wet to water wet and the related Pickering emulsion can be used for Chemical Enhanced Oil Recovery (C-EOR). According to the interfacial tension results presented in Fig. 11, the related amount for (a) water droplet as reference sample and the nanofluid droplets of (b) 70% MWCNT/SiO_2 nano hybrid and (c) 70% nanoporous graphene/SiO_2 nanohybrid are 53.90, 30.04 and 29.82 mN/m respectively. The maximum amount is related to the injection of water droplet and the minimum amount is related to the injection of nanofluid droplet of 70% nanoporous graphene/SiO_2 Nano hybrid. This result indicates better ability of 70% nanoporous graphene/SiO_2 nanohybrid for decreasing the interfacial tension in comparison with the other samples.

We suppose that the preference of nanoporous graphene to MWCNT and graphite for preparing silica nanohybrid Pickering emulsion is related to the multilayer structure of nanoporous graphene. Also in treatment step with Nitric acid, functionalized nanoporous graphene has several kinds of oxidation groups such as carboxyl, epoxy and hydroxyl at the edges [35]. Therefore, functionalized nanoporous graphene has an amphiphile surface with hydrophilic edges and hydrophobic plane [36]. Formation of such functional groups on the layer structure of nanoporous graphene is exceeded in comparison to MWCNT and graphite. Therefore, nanoporous graphene can reacts with more amounts of Silica nanoparticles and the related Pickering emulsion will be more stable at the oil reservoirs conditions. Also the layer structure of nanoporous graphene can better spread on the reservoir outcropping rock in comparison to Multi Walled Carbon Nanotubes (MWCNT) and graphite.

For estimation of functional groups amount that were formed on the desired carbon structure, the FTIR spectrum and surface pH analysis can be utilized. Formation of carboxylic acid functional group causes the surface pH diminishes. Obviously, the more carboxylic acid formation leads to more activity of carbon structure and formation of Pickering emulsion with better properties for Chemical Enhanced Recovery (C-EOR).

Surface pH [44] results of the functionalized forms of nanoporous graphene, Multi-Walled Carbon nanotube and graphite are about 4.52, 5.58 and 5.95, respectively. Also as Fig. 12 shows the FTIR spectrums of the mentioned functionalized carbon structures, the intensity of the carboxylic acids peaks (3433 cm^{-1} and 1623 cm^{-1}) on the functionalized nanoporous graphene is more than the others. All of these results indicate that the formation of acidic functional groups on the functionalized nanoporous graphene is more than the functionalized forms of Multi-Walled Carbon nanotubes and graphite.

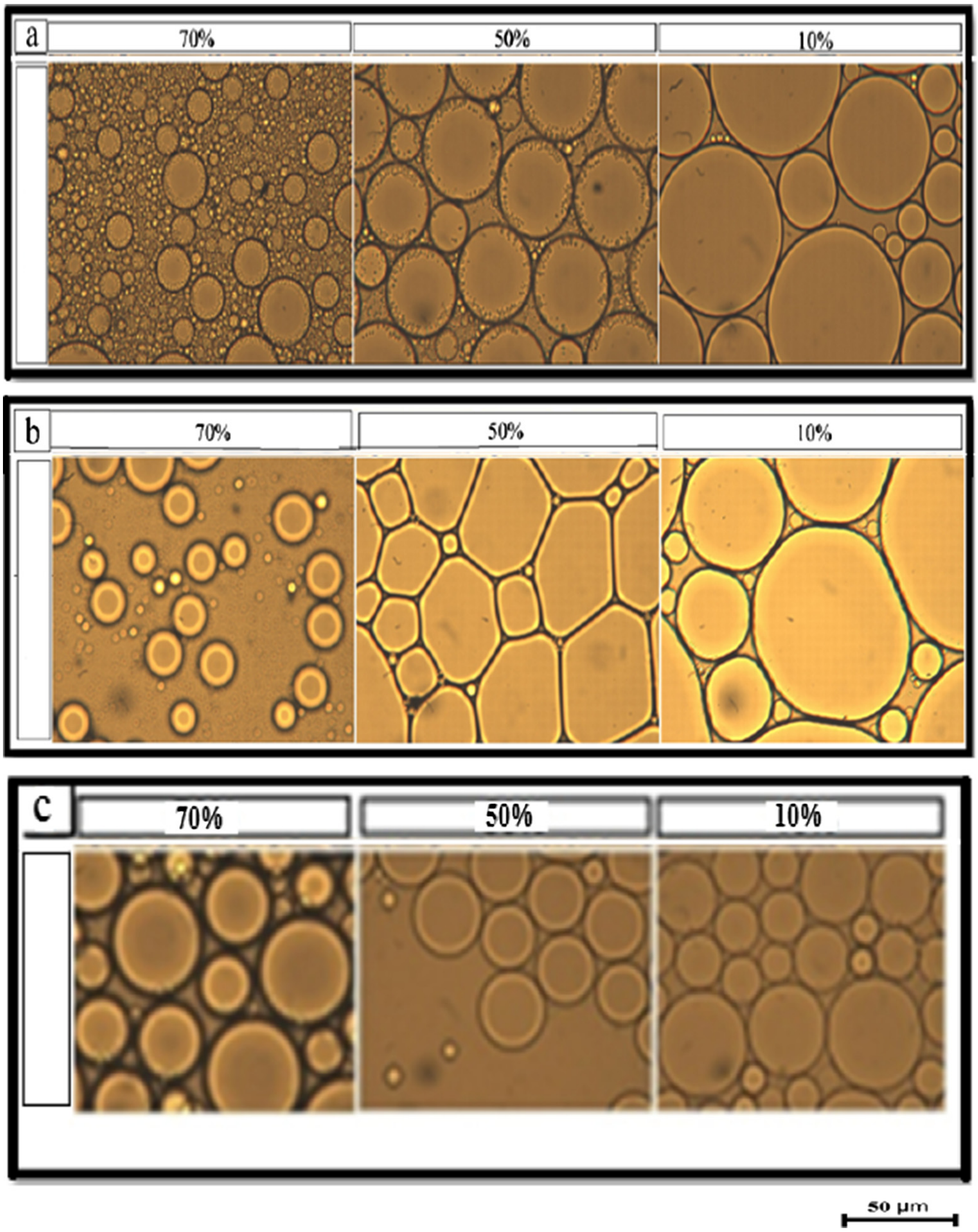


Fig. 6. Emulsion phase optical microscopic images of (a) graphite/SiO_2 nanohybrid Pickering emulsions (b) nanoporous graphene nanohybrid Pickering emulsions (c) MWCNTs /SiO_2 nanohybrid Pickering emulsions.

Polymers have been widely used in different enhanced oil recovery (EOR) applications as a mobility improver, the ability of nanomaterials for improving the rheological behaviour of polymer suspensions has been reported in literature [20]. Generally, Polyacrylamides (PAM) and its derivatives are used in polymer EOR processes. In aqueous solutions, the amide groups present in polymer molecule immediately hydrolyzed into carboxylic group, which reacts with the ions presents in solution and as a result, the viscosity is decreased, and also in severe condition, it even leads to the precipitation. The commonly used polysaccharide is xanthan gum (XG), which is a bacterial polysaccharide .Compared with the PAM, xanthan gum (XG) has a more rigid structure and also it has relatively non-ionic behaviours. These properties make this polysaccharide relatively insensitive to salinity and hardness. However, it is susceptible to the bacterial degradation after it has been injected into the field [1].

In this research, we have tried to find out the effect of nanoporous graphene/silica nanohybrid particle on the rheological behaviour of xanthan gum (XG) suspension. Rheological experiments were performed on nanoporous graphene/SiO_2 nano hybrid/xanthan gum (XG) suspension and compared with those of pure xanthan gum (XG) suspension.

In terms of rheology, fluids are classified as Newtonian and Non-Newtonian fluids. If the plot of shear stress versus shear rate at a given temperature is a straight line, the fluid has Newtonian behaviour, and the constant slop of the plot is the fluid apparent viscosity. The fluid that does not obey the Newtonian relationship between the shear stress and shear rate is called non-Newtonian. Liquids such as polymer melts, polymer solutions and liquids in which fine particles are suspended (slurries and pastes) are usually non-Newtonian. In this case, the slope of the shear stress versus shear rate curve will not be constant. If the viscosity decreases

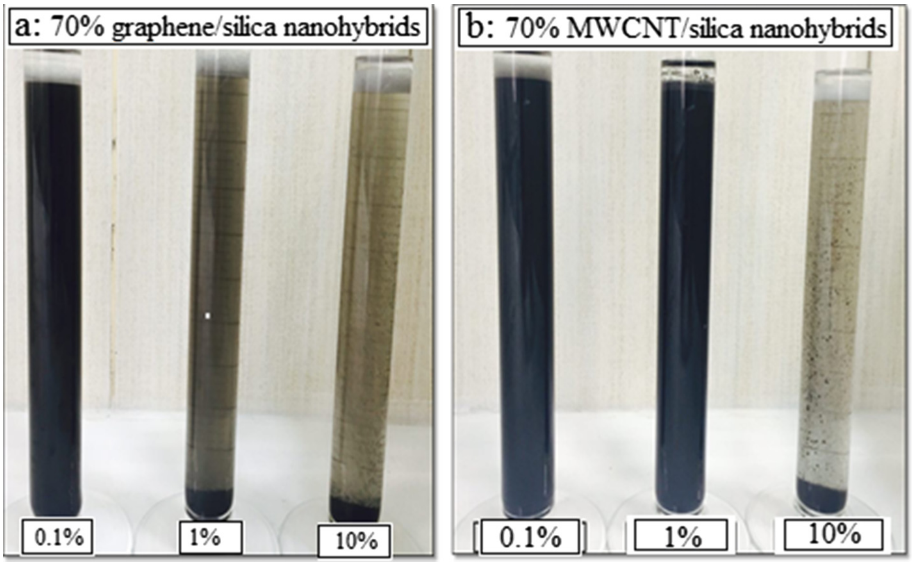


Fig. 7. Stability evaluation of (a) 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions and (b) 70% MWCNT/SiO_2 nanohybrid emulsion at different salinities (0.1%, 1% and 10%).

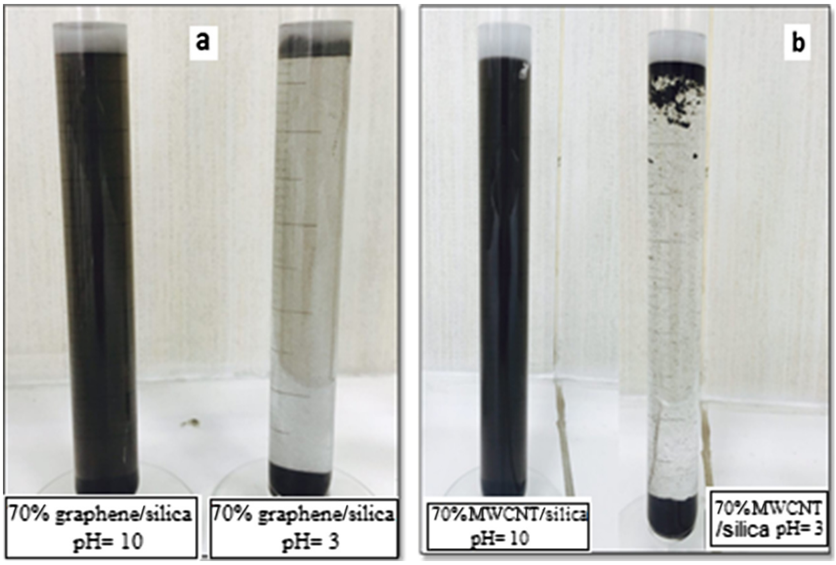


Fig. 8. Stability evaluation of (a) 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions and (b) 70% MWCNT/SiO_2 nanohybrid Pickering emulsion at different pH (3,10).

with increasing shear rate, the fluid is called shear-thinning. If the viscosity increases with increasing shear rate, the fluid is called shear- thickening. Shear-thinning behaviour is more common than shear-thickening. Shear-thinning fluids also are called pseudo plastic fluids. Drilling fluids must be shear thinning fluids for removing cuttings from the oil well because of lower viscosity at high-shear rates and higher viscosity at low-shear rates which are efficient for hole cleaning. This property is very suitable for drilling when minimum pressure losses are required for the high-shear conditions inside the narrow bore of the drill string. Higher viscosity is wanted in the low-shear conditions of the larger bore of the drill string.

Fig. 13 represents (a) effect of the nanoporous graphene/SiO_2 nanohybrid with different concentrations on the rheological behaviour of the nanoporous graphene/SiO_2 nanohybrid/xanthan gum (XG) suspension with 2500 ppm xanthan gum (XG) concentration and (b) Apparent viscosity changes in different concentrations of the nanoporous graphene/SiO_2 nanohybrid with shear rate addition (c) relative increase in viscosity of nanoporous graphene/SiO_2 nanohybrid/xanthan gum (XG) suspension versus increasing concentration of nanoporous graphene/SiO_2 nanohybrid in 2500 ppm xanthan gum (XG) concentration. With attention to the Fig. 13, it can be concluded that all of the desired fluids are thinning fluid and have non-Newtonian behaviour (i.e., the viscosity continuously decreased with increasing shear rate) [20].

It can be seen that the decrease in viscosity in case of nanoporous graphene/SiO_2 nanohybrid/xanthan gum (XG) suspension is less than that in case of xanthan gum (XG). Results demonstrated that nanoporous graphene/SiO_2 nanohybrid can improve the rheological behaviour of xanthan gum (XG) suspension. An interesting quality of polymers is to encourage bridging induced flocculation of nanoparticles which are present in water, are finally leads to

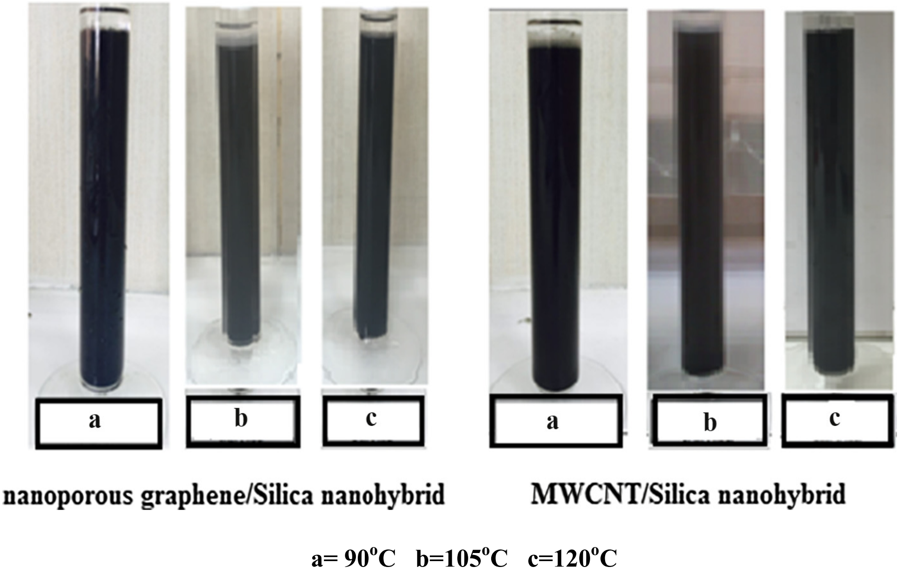


Fig. 9. Stability evaluation of 70% nanoporous graphene/SiO_2 nanohybrid Pickering emulsions and 70% MWCNT/SiO_2 nanohybrid emulsion at several oil reservoir temperatures such as (a) 90 °C, (b)105 °C and (c)120 °C.

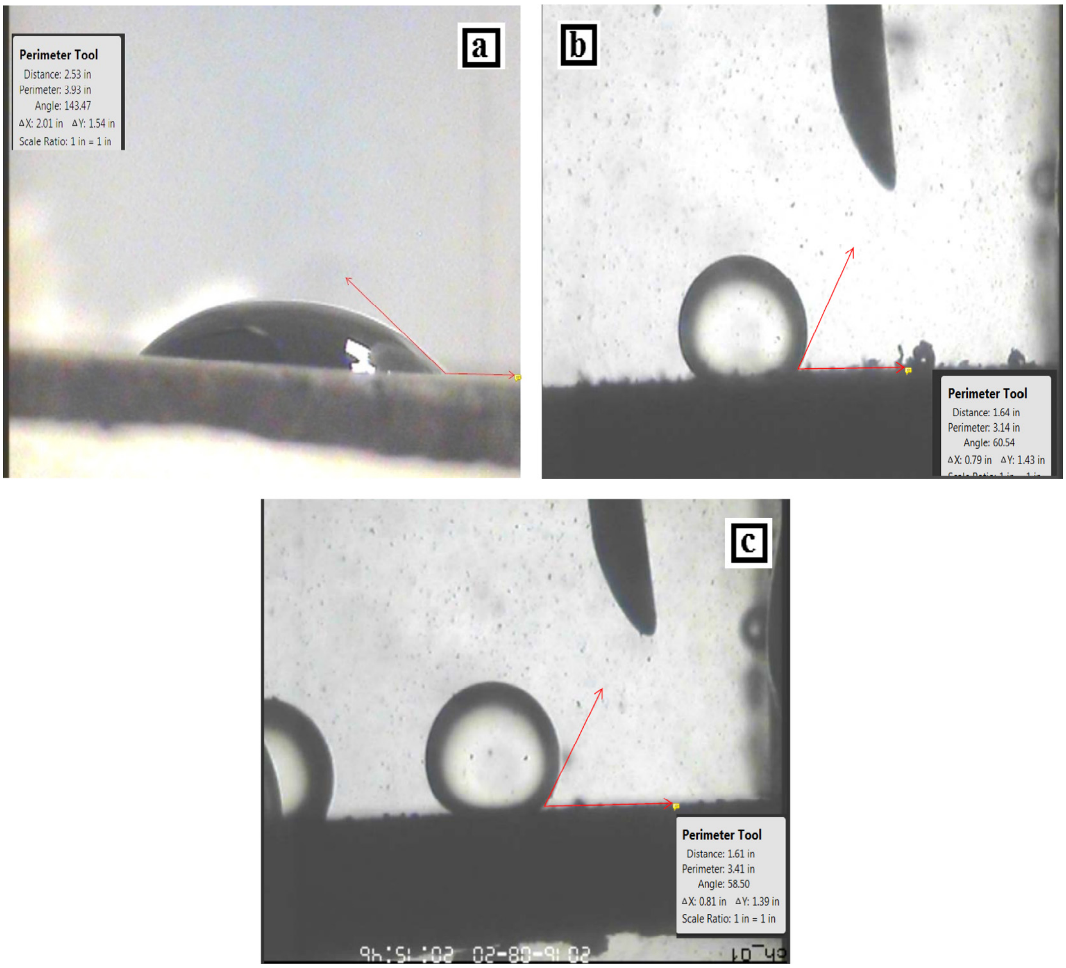


Fig. 10. Contact angle between (a) water droplet and carbonate rock reservoir as reference sample (b) water droplet and stone reservoir with a layer of 70% MWCNT/silica nanohybrid (c) water droplet and stone reservoir with a layer of 70% nanoporous graphene/Silica nanohybrid.

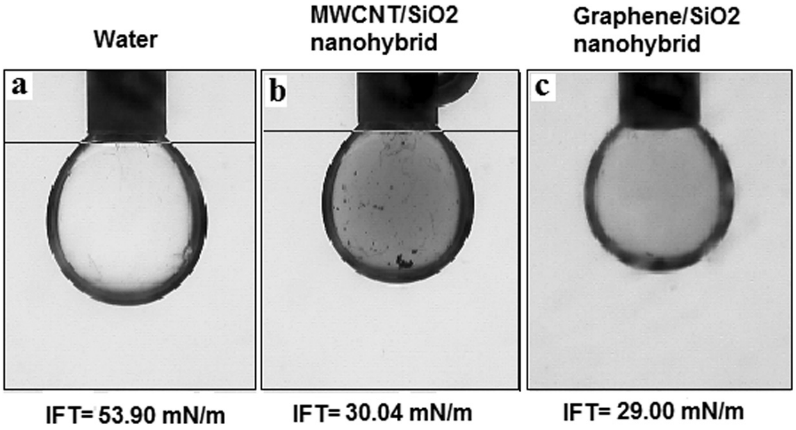


Fig. 11. Interfacial tension results related to (a) water droplet as reference sample and the nanofluid droplets of (b) 70% MWCNT/SiO_2 Nano hybrid and (c) 70% nanoporous graphene/SiO_2 nanohybrid.

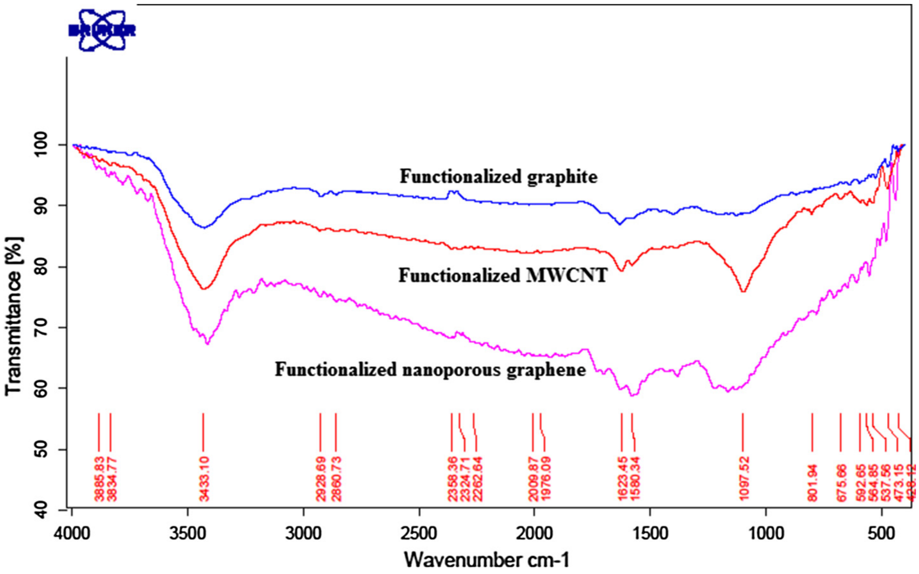


Fig. 12. FTIR spectrum of the functionalized nanoporous graphene, MWCNT and graphite.

the improved rheological property [20]. When a nanoporous graphene/SiO_2 nanohybrid particle was added in xanthan gum (XG), it was found that it alters the properties of xanthan gum (XG) solution and increases the viscosity and elasticity of the mentioned solution [20]. Rheological measurements were taken under steady shear to calculate the steady properties. The nanoporous graphene/SiO_2 nanohybrid/xanthan gum (XG) suspensions describe a non-Newtonian, shear thinning behaviour (i.e., the viscosity continuously decreased with increasing shear rate) [20]. The incremental viscosity and shear thinning behaviour of this suspension can be attributed to the strong interaction between xanthan gum (XG) and nanoporous graphene/SiO_2 nanohybrid particles in water. The polymer chain is physically bounded at the surface of nanoporous graphene/SiO_2 nanohybrid particles. In fact the nanoporous graphene/SiO_2 nanohybrid particle acts as a physical cross-linker between different polymeric chains. During adsorption, a polymer chain may be attached to more than one particle at the same time and also a number of polymeric chains can be adsorbed on the surface of a particle which is usually irreversible. Upon adsorption, only a portion of polymeric chain is in direct contact of nanoporous graphene/SiO_2 nanohybrid surface at single or several points, while the rest (tail) extend away from the surface into the solution. These tails get adsorbed onto one or different nanoporous graphene/SiO_2 nanohybrid particle when it comes into contact surface of nanoporous graphene/SiO_2 nanohybrid. These results in flocculation mechanism of nanoporous graphene/SiO_2 nanohybrid particle and a micelle type formation and analysing of the three-dimensional network of flocks are deducted. Because of the irreversible adsorption of polymer, the resultant stable macromolecular structure is not easily broken and it leads to the enhancement of the increase in suspension viscosity [20].

In our previous study [48], we have improved the preference of MWCNT/ SiO_2 nanohybrid Pickering emulsion to similar emulsions of SWCNT and activated carbon for chemical enhanced oil recovery. In this research we have completed and improved our research in this field and demonstrated that the properties of nanoporous graphene/SiO_2 nanohybrid Pickering emulsion is superior to the MWCNT/ SiO_2 nanohybrid Pickering emulsion for applying in Chemical Enhanced Oil Recovery (C-EOR) and the nano porous graphene/SiO_2 nanohybrid can improve the rheological behaviour of a polymer suspensions that are suitable for polymer flooding technique.

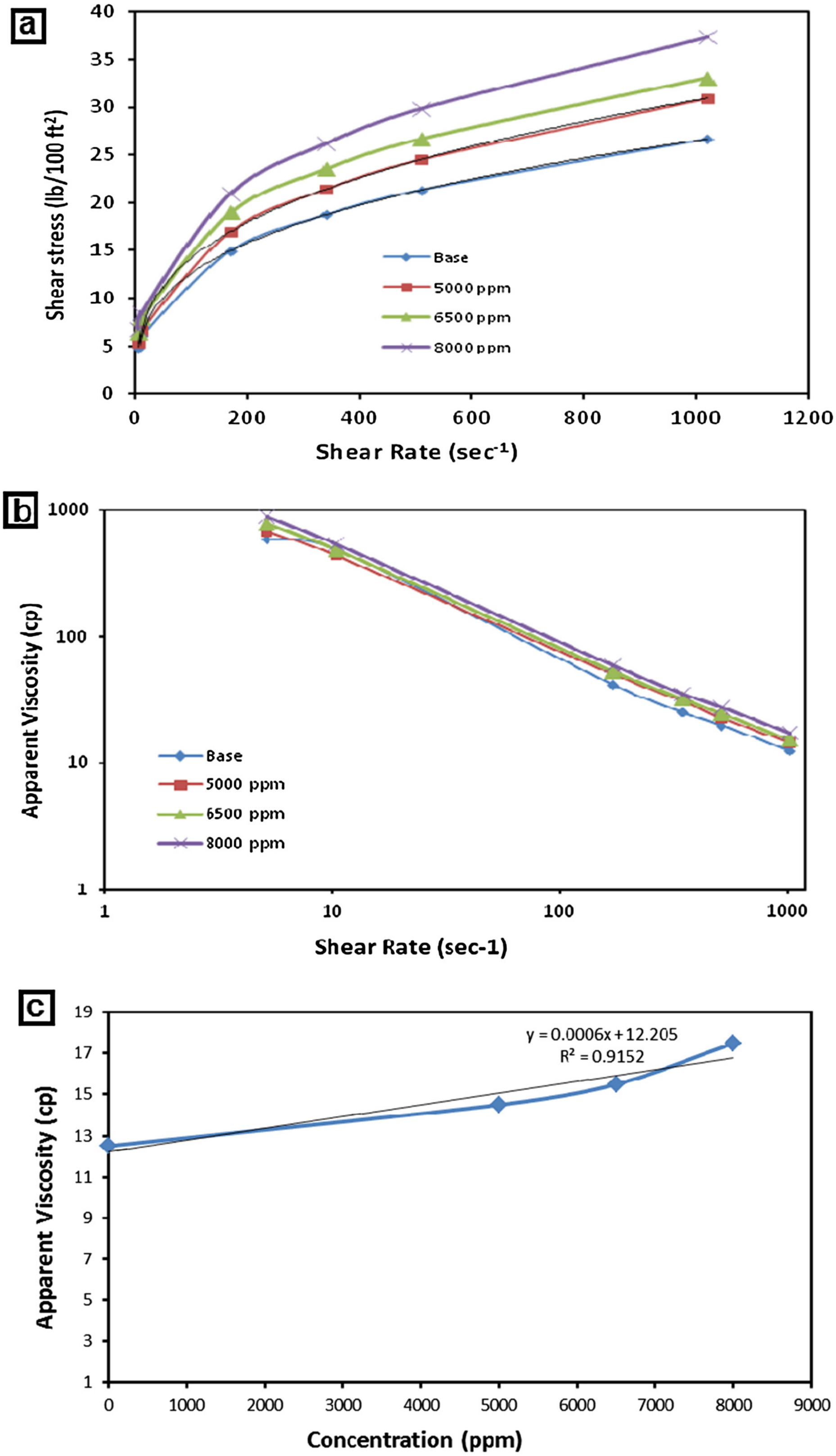


Fig. 13. (a) effect of the nanoporous graphene/SiO_2 nanohybrid with different concentrations on rheological behaviour of the nanoporous graphene/SiO_2 nanohybrid /xanthan gum (XG) suspension with 2500 ppm xanthan gum (XG) concentration and (b) Apparent viscosity changes in different concentrations of the nanoporous graphene/SiO_2 nanohybrid with shear rate addition (c) relative increase in viscosity of nanoporous graphene/SiO_2 nanohybrid /xanthan gum (XG) suspension versus increasing concentration of nanoporous graphene/SiO_2 nanohybrid in 2500 ppm xanthan gum (XG) concentration.

5. Conclusion

In this research, facile and economical preparation method of nanoporous graphene/silica nanohybrid was proposed and for evaluation of the mentioned Pickering emulsion in comparison to the similar nanohybrids, different carbon structures nanohybrids with SiO_2 nanoparticles with different weight percent are prepared. The as-prepared nanomaterials were characterized with X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and Thermal Gravimetric Analysis (TGA).

Pickering emulsions of these nanohybrids were prepared with n-Octane as an oil model, suitable anionic surfactant (such as SDBS) and 2-Propanol as an alcoholic co-surfactant at the pH = 7 in ambient temperature and with distilled water. Stability of the mentioned Pickering emulsions was controlled for one month. Emulsion phase morphology was investigated with optical microscopic images. Evaluation results demonstrated that the best samples are 70% MWCNT/SiO_2 and 70% nanoporous graphene/SiO_2 nanohybrids. Stability of the selected nanohybrids was investigated by alteration of salinity, pH and temperature. The results displayed that the related Pickering emulsions of the selected nanohybrids have very good stability at 1% salinity, at the ambient and oil reservoir temperatures (90 °C, 105 °C and 120 °C) and neutral and alkaline (7,10) pH that is suitable for the oil reservoirs conditions. Contact angle results highlighted that the nanoporous graphene/SiO_2 nanohybrid is more effective for improvement of the reservoir outcrop wettability alteration from oil-wet to water-wet in comparison to the other samples. Interfacial tension evaluations indicate that the maximum amount is related to the injection of water droplet and the minimum amount is related to the injection of nanoporous graphene/SiO_2 nanohybrid nanofluid droplet. This result indicates the nanoporous graphene/SiO_2 nanohybrid can better reduce the interfacial tension in comparison with the other samples. Our results demonstrated that the nanoporous graphene/SiO_2 nanohybrids Pickering emulsion has superior properties to the MWCNT/SiO_2 nanohybrids Pickering Emulsion for Chemical Enhanced Oil Recovery (C-EOR) and the nano porous graphene/SiO_2 nanohybrid can improve the rheological behaviour of polymer suspensions suitable for polymer flooding technique.

Acknowledgment

The authors are grateful from Research Institute of Petroleum Industry for its support of this research.

References

[1] Mandal A. Chemical flood enhanced oil recovery: a review. Int J Oil Gas Coal Technol 2015;9:241–64.

[2] Larson RG, Davis HT, Scriven LE. Displacement of residual nonwetting fluid from porous media. Chem Eng Sci 1980;36:75–85.

[3] Wang J, Dong M, A laboratory study of polymer flooding for improving heavy oil recovery. In: Proceedings of Canadian International Petroleum Conference, SPE; 2007.

[4] Wang J, Yuan S, Shen P, Zhong T, Jia X. Understanding of fluid flow mechanism in porous media of EOR by ASP flooding from physical modeling. In: International Petroleum Technology Conference, Dubai; 2007. p. 11257.

[5] Clark SR, Pitts MJ, Smith SM. Design and application of an alkaline-surfactant polymer recovery system to the West Kiehl. In: SPE 17538 presented at the SPE Rocky Mountain Regional Meeting, Casper, WY; 1988, p. 515–522.

[6] Marmur A. Equilibrium contact angles theory and measurement. Colloids Surf A 1996;116:55–61.

[7] Demin W, Jiecheng C, Junzheng W, Zhenyu Y, Hongfu L. Summary of ASP pilots in Daqing oil field. In: SPE57288 presented at the Asia Pacific Improved Oil Recovery Conference, Kuala Lumpur, Malaysia; 1999.

[8] Elraies KA, Tan IM, Awang M, Fathaddin MT. A new approach to low-cost, high performance chemical flooding system. In: SPE 133004 presented at the SPE Production and Operation Conference and Exhibition, 8–10 June, Tunis, Tunisia; 2010.

[9] Kumar R, Mohanty KK. ASP flooding of viscous oils. In: SPE 135265 presented at the SPE Annual Technical Conference and Exhibition, 19–22 September, Florence, Italy; 2010.

[10] Southwick JG, Svec Y, Chilek G, Shahin GT. The effect of live crude on alkaline-surfactant-polymer formulations: implications for final formulation design. In: SPE-135357 presented at the SPE Annual Technical Conference and Exhibition in Florence, 20–22 September, Italy; 2010.

[11] Santanna VC, Curbelo FDS, Castro Dantas TN, Dantas Neto AA, Albuquerque HS, Garnica AIC. Microemulsion flooding for enhanced oil recovery. J Pet Sci Eng 2009;66:17–120.

[12] Pickering SU. Emulsions. J Chem Soc Trans 1907;91:2001–21.

[13] Ramsden W. Separation of solids in the surface-layers of solutions and 'suspensions' (observations on surface-membranes, bubbles, emulsions, and mechanical coagulation). Preliminary account. R Soc London 1903-1904;72:156–64.

[14] Melle S, Lask M, Fuller GG. Pickering emulsions with controllable stability. Langmuir 2005;21:2158–62.

[15] Binks BP, Clint JH. Solid wettability from surface energy components: relevance to Pickering emulsions. Langmuir 2002;18:1270–3.

[16] Bon SAF, Colver P. Pickering mini emulsion polymerization using laponite clay as a stabilizer. Langmuir 2007;23:8316–22.

[17] Calderon FL, Schmitt V. Solid- stablized emulsions. Curr Opin Colloid Interface Sci 2008;13:217–27.

[18] Tang M, Wang X, Wu F, Liu Y, Zhang S, Pang X, Li X, Qiu H. Au nanoparticle/graphene oxide hybrids as stabilizers for Pickering emulsions and Au nanoparticle/graphene oxide@polystyrene microspheres. Carbon 2014;71:238–48.

[19] Ershadi M, Alaei M, Rashidi A, Ramazani A, Khosravani S. Carbonate and sandstone reservoirs wettability improvement without using surfactants for Chemical Enhanced Oil Recovery (C-EOR). Fuel 2015;153:408–15.

[20] Kumar Maurya N, Mandal A. Studies on behavior of suspension of silica nanoparticle in aqueous polyacrylamide solution for application in enhanced oil recovery. Pet Sci Technol 2016;34:429–36.

[21] Shen M, Resasco DE. Emulsions stabilized by carbon nanotube-silica nanohybrids. Langmuir 2009;25:10843–51.

[22] Barthet C, Hickey AJ, Cairns DB, Armes SP. Synthesis of novel polymer-silica colloidal nanocomposites via free-radical polymerization of vinyl monomers. Adv Mater 1999;11:408–10.

[23] Percy MJ, Barthet C, Lobb JC, Khan MA, Lascelles SF, Vamvakaki M, et al. Synthesis and characterization of vinyl polymer−silica colloidal nanocomposites. Langmuir 2000;16:6913–20.

[24] Villamizar LC, Lohateeraparp P, Harwell JH, Resasco DE, Shiau BJB. Interfacially active SWNT/silica nanohybrid used in enhanced oil recovery. In: SPE Improved Oil Recovery Symposium, 24-28 April, Tulsa, Oklahoma, USA; 2010.

[25] Zhang NN, Qiu HX, Liu Y, Wang W, Li Y, Wang XD, et al. Fabrication of gold nanoparticle/graphene oxide nanocomposites and their excellent catalytic performance. J Mater Chem 2011;21:11080–3.

[26] Kim JD, Palani T, Kumar MR, Lee SW, Choi HC. Preparation of reusable Ag decorated graphene oxide catalysts for decarboxylative cycloaddition. J Mater Chem 2012;22:20665–70.

[27] Giovanni M, Poh HL, Ambrosi A, Zhao GJ, Sofer Z, Sanek F, et al. Noble metal (Pd, Ru, Rh, Pt, Au, Ag) doped graphene hybrids for electrocatalysis. Nanoscale 2012;4:5002–8.

[28] Chen XM, Wu GH, Chen JM, Chen X, Xie ZX, Wang XR. Synthesis of "clean" and well-dispersive Pd nanoparticles with excellent electrocatalytic property on graphene oxide. J Am Chem Soc 2011;133:3693–5.

[29] Tang M, Wu T, Xu X, Zhang L, Wu F. Factors that affect the stability, type and morphology of Pickering emulsion stabilized by silver nanoparticles/graphene oxide nanocomposites, mater. Res Bull 2014;60:118–29.

[30] Lightcap IV, Kosel TH, Kamat PV. anchoring semiconductor and metal nanoparticles on a two-dimensional catalyst mat. Storing and shuttling electrons with reduced graphene oxide. Nano Lett 2010;10:577–83.

[31] Goncalves G, Marques PAAP, Granadeiro CM, Nogueira HIS, Singh MK. Surface modification of graphene nanosheets with gold nanoparticles: the role of oxygen moieties at graphene surface on gold nucleation and growth. J Gracio Chem Mater 2009;21:4796–802.

[32] Si Y, Samulski ET. Exfoliated graphene separated by platinum nanoparticles. Chem Mater 2008;20:6792–7.

[33] Scheuermann GM, Rumi L, Steurer P, Bannwarth W, Mülhaupt R. Palladium nanoparticles on graphite oxide and its functionalized graphene derivatives as highly active catalysts for the Suzuki-Miyaura coupling reaction. J Am Chem Soc 2009;131:8262–70.

[34] Park S, Ruoff RS. Chemical methods for the production of graphened. Nat Nanotechnol 2009;4:217–24.

[35] Segal M. Selling graphene by the ton. Nat Nanotechnol. 2009;4:612–4.

[36] Kou L, Gao C. Making silica nanoparticle-covered graphene oxide nanohybrids as general building blocks for large-area superhydrophilic coatings. Nanoscale 2011;3:519–28.

[37] Kim JY, Cote LJ, Kim F, Yuan W, Shull KR, Huang JX. Graphene oxide sheets at interfaces. J Am Chem Soc 2010;132:8180–6.

[38] Tan R, Li CY, Luo JQ, Kong Y, Zheng WG, Yin DH. An effective heterogeneous L-proline catalyst for the direct asymmetric aldol reaction using graphene oxide as support. J Catal 2013;298:138–47.

[39] Mayavan S, Jang HS, Lee MJ, Choi SH, Choi SM. Enhancing the catalytic activity of Pt nanoparticles using poly sodium styrene sulfonate stabilized graphene supports for methanol oxidation. J Mater Chem A 2013;1:3489–94.

[40] Muhammad S, Chandra V, Kemp KC, Kim KS. Synthesis of N-doped microporous carbon via chemical activation of polyindole- modified graphene oxide sheets for selective carbon dioxide adsorption. Nanotechnology 2013;24:255702–9.

[41] Mi X, Huang GB, Xie WS, Wang W, Liu Y, Gao JP. Preparation of graphene oxide aerogel and its adsorption for Cu^{2+} ions. Carbon 2012;50:4856–64.

[42] Liu Y, Ma JK, Wu T, Wang XR, Huang GB, Liu Y. A Cost effective reduced graphene oxide-coated polyurethane sponge as a highly efficient and reusable oil-absorbent. ACS Appl Mater Interfaces 2013. http://dx.doi.org/10.1021/am4024252.

[43] Tajik S, Nasernejad B, Rashidi AM. Preparation of silica-graphene nanohybrid as a stabilizer of emulsions. J Mol Liq 2016;222:788–95.

[44] Fallah RN, Azizian S. Removal of thiophenic compounds from liquid fuel by different modified activated carbon cloths. Fuel Process Technol 2012;93:45–52.

[45] Rao CNR, Biswas K, Subrahmanyam KS, Govindaraj A. Graphene, the new nanocarbon. J Mater Chem 2009;19:2457–69.

[46] JabariSeresht R, Jahanshahi M, Rashidi AM, Ghoreyshi AA. Fabrication and evaluation of nonporous graphene by a unique spray pyrolysis method. Chem Eng Technol 2013;36:1–10.

[47] Zhang T, Davidson D, Bryant SL, Huh C. Nanoparticle-stabilized emulsions for applications in enhanced oil recovery. In: SPE improved oil recovery symposium, 24–28 April, Tulsa, Oklahoma, USA; 2010.

[48] AfzaliTabar M, Alaei M, Ranjineh Khojasteh R, Motiee F, Rashidi AM. Preference of multi-walled carbon nanotube (MWCNT) to single-walled carbon nanotube (SWCNT) and activated carbon for preparing silica nanohybrid pickering emulsion for chemical enhanced oil recovery (C-EOR). J Solid State Chem 2016;245:164–73.