

# Automatic dispersion, long-term stability of multi-walled carbon nanotubes in high concentration electrolytes

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**Abstract** Nanoparticles have been known as the useful materials in working fluids for petroleum industry. But the stabilization of nano-scaled materials in water-based working fluids at high salinities is still a big challenge. In this study, we successfully prepared the anionic polymer/multi-walled carbon nanotubes (MWNTs) composites by covalently wrapping of MWNTs with poly (sodium 4-styrenesulfonate) (PSS) to improve the stability of MWNTs in high concentration electrolytes. The PSS/MWNTs composites can automatically disperse in salinity up to 15 wt% NaCl and API brines (8 wt% NaCl + 2 wt%

CaCl<sub>2</sub>). Hydrodynamic diameters of composites were measured as a function of ionic strength and API brines by dynamic light scattering (DLS). By varying the concentration of brines, hydrodynamic diameter of PSS/MWNTs composites in brines fluctuated between  $545 \pm 110$  nm for 14 days and  $673 \pm 171$  nm for 30 days. Above results showed that PSS/MWNTs could be well stable in high salts solutions for a long period of time. After wrapped with PSS, the diameters of nanotubes changed from 30 ~ 40 to ~ 430 nm, the thickness of wrapped polymer is about ~ 400 nm by analysis of morphologies. The zeta potentials of PSS/MWNTs composites in various salinity of brines kept at approximately  $-41 \sim -52$  mV. Therefore, the well dispersion of PSS/MWNTs in high salinity is due to large negative charges of poly (sodium 4-styrenesulfonate), which provide enough electrostatic repulsion and steric repulsion to hinder compression of electric double layer caused by high concentration electrolytes.

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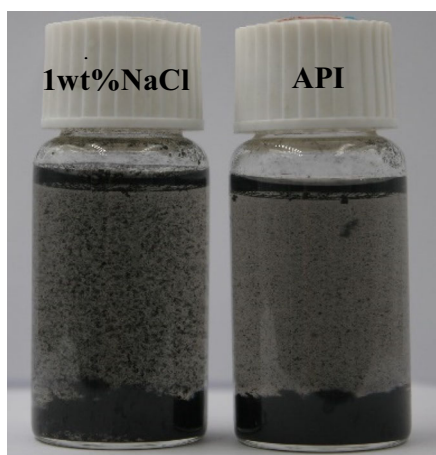
**Keywords** Multi-walled carbon nanotubes · Anionic polymer · Poly (sodium 4-styrenesulfonate) · Colloid stability · Concentrated brines · Petroleum industry applications

## Introduction

Nanoparticles are attention-attracting materials in oil and gas industry (Cai et al. 2012; Contreras et al. 2014; Ghanbari et al. 2016), and it have been reported in a wide range of applications such as micro-nanometer particle plugging (Barry et al. 2015;

Kosynkin et al. 2012), enhancing oil recovery (Luo et al. 2016; Luo et al. 2017), oil-based lubricates (Zhang et al. 2017), and downhole hydrocarbon detection (Hwang et al. 2012).

Nanoparticles are always exposed to brine environment in most of the applications for the petroleum industry, such as the oil reservoirs, which usually contains high salinity. Nanoparticles are inclined to agglomerate into larger particles in salt solutions, losing the unique properties of nanomaterials. For example, nanoparticles (NPs) as fluid loss additives were added into water-based drilling fluids for plugging micro-nanometer pore and throat, nanoparticles will become larger size and loss them functions. Therefore, nanoparticles cannot keep at nanoscale when it is added into the working fluids containing salts. Dan Luo (Luo et al. 2017) and their group firstly prepared graphene-based amphiphilic Janus nanosheets and investigated the colloidal stability of nanosheets at different salt concentrations. Their studies showed that graphene-based amphiphilic Janus nanosheets could not disperse in salt solution, even in 0.05844 wt% NaCl solution. As shown in Fig. 1, uncoated multi-walled nanotubes aggregated almost immediately after being dispersed in both 1.0 wt% NaCl solutions and the standard API brines. It reveals that multi-walled carbon nanotubes (MWNTs) was not stably dispersed even in low salinity of 1.0 wt% NaCl solutions and the standard API brines at room temperature (Fig. 1). This was attributed to the presence of salts, which could easily



**Fig. 1** Unstable mixtures of MWNTs in 1.0 wt% NaCl solutions and API brines at initial preparation (the concentration of dispersion both were 1 mg/ml)

disrupt electric double layers between particles and make nanoparticles unstable (Elimelech and O'Melia 1990; Kharissova et al. 2013). Thus, stabilization of nano-sized materials in aqueous environments with high salinities is an ongoing important issue for petroleum industry.

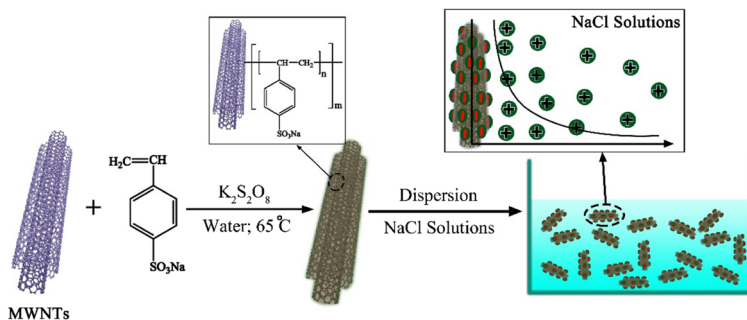
In recent years, surfactants (Duque et al. 2008), polymers (Kadhun et al. 2017), and small ligands (Kotsmar et al. 2010) used to stabilize nanoparticles in brines have been reported. Surfactants, which adsorb onto nanoparticles by hydrophobic components and extend their hydrophilic components into brines, are providing steric stabilization (Jones et al. 1991). Sodium dodecyl sulfate (SDS) is applied to make single-walled carbon nanotubes stable in NaCl concentrations of 200 mM, and MgCl<sub>2</sub> concentrations of 10 mM brines for 24 h. Glaura G.Silva (Soares et al. 2014) mentioned that AvanelS 150 CGN surfactant (C<sub>12-15</sub>(EO)<sub>15</sub>SO<sub>3</sub><sup>-</sup>Na<sup>+</sup>) was used as a surfactant for stable dispersions of the modified carbon nanoparticles in saline water. Polyvinyl pyrrolidone is a highly water-soluble polymer, which adsorbed onto the CNTs surface to provide steric stabilization by long chains in water repelling each other. But CNTs-PVP showed lower long-term stability in electrolytes than in salt-free solution (Ntim et al. 2011). Zhifeng Ren (Luo et al. 2016) showed that sequential addition of polyvinyl pyrrolidone and polyvinyl alcohol was applied to stabilize graphene-based amphiphilic Janus in a saline environment for a certain time before reaching to underground reservoirs. But in above methods, nanoparticles do not disperse in electrolytes automatically, instead of adding extensive surfactants and polymer stabilizers. Moreover, it usually needs very high concentration of stabilizer (polymers and surfactants) to make nanoparticles dispersion stable, which is inconvenient for further practical application.

Studies show that grafting polyelectrolyte on nanoparticles is an effective way to stabilize nanoparticles in salt solution. Christopher Griffith (Griffith and Daigle 2017) attachment 24 wt% of 100,000 Da polyvinyl alcohol to the biochar particle surface, which was stable in synthetic sea water for over 1 month with mean particle size of ~330 nm. James M. Tour (Hwang et al. 2012) studied that sulfated polyvinyl alcohol functionalized carbon black nanoparticles could stable in synthetic seawater and API brines at 100 °C, but polyvinyl alcohol

functionalized carbon black was not stable in API brines. Johnston et al. (Bagaria et al. 2013) showed that iron oxide nanoparticles (NPs) covalently grafted with poly(2-acrylamido-2-methylpropanesulfonate-co-acrylic acid) could effectively stabilize the nanoparticles in standard American Petroleum Institute (API) brine for 1 month.

Our study aimed to improve the stability of MWNTs dispersed in salts solution and make the automatic dispersion come true. Based on the previous studies, anionic polymers especially containing sulfonate have good effect on improving stability of nanoparticles in salt solutions. PSS is one kind of sulfonated polymers, which were shown to be soluble in relatively concentrated solutions of electrolytes due to numbers of sulfonated groups (Bagaria et al. 2013). Sulfonated groups inclined to be hydrated in aqueous solution and own negative charges, which can be soluble in electrolytes (Zheng et al. 2014). Here, we employed a facile one-pot method to covalently wrap MWNTs with poly (sodium 4-styrenesulfonate) (PSS), which can stabilize MWNTs in brine solution indefinitely. The method is illustrated in Scheme 1. The stability of the multi-walled nanotube in brines was ascribed to these negatively charged sulfated polyelectrolytes (PSS), which carry high net charges providing sufficient electrostatic repulsion even in a high ionic strength environment. The dispersion stability of PSS/MWNTs in brines and API brines were monitored by both visually and spectroscopically. Dynamic light scattering (DLS) was used to monitor changes of hydrodynamic diameter for composites. After modification, MWNTs could be stable in API brines and up to salinity of 15 wt% NaCl. Grafting highly charged polyelectrolytes on MWNTs surfaces to overcome the compression of electric double layer by electrolytes.

**Scheme 1** The PSS/MWNTs composites dispersed in electrolyte solution



## Experimental section

### General materials and methods

Multi-walled carbon nanotubes (diameter of 20–30 nm, lengths of 10–30  $\mu\text{m}$ , purity 95%) were purchased from Chengdu Institute of Organic Chemistry, Chinese Academy of Sciences. Potassium persulfate (purity 99.99%, metals basis) and sodium 4-styrenesulfonate (purity 90%) were purchased from Aladdin (China). Sodium chloride (AR, 99.5%) and calcium chloride (AR, 99.5%) were purchased from Kelong company (Chengdu). Poly (sodium 4-styrenesulfonate) (MW = 70 kDa) was purchased from Alfa Aesar (China). All chemicals were used as received without further purification.

### Synthesis of poly (sodium 4-styrenesulfonate) covalently wrapped multi-walled carbon nanotube

PSS/MWNTs were prepared by in situ free radical polymerization (Shuhui Qin et al. 2004). A mixture of 50 mg of pristine multi-walled carbon nanotubes, 5.0 g of sodium 4-styrenesulfonate (NaSS), and 50 mg of potassium persulfate as a free radical initiator was stirred at 65  $^{\circ}\text{C}$  for 48 h. The reaction was protected by argon all the time. After reaction, amorphous carbon and catalyst residues were removed by centrifugation, and excess unbound PSS was removed by filtration. Then PSS/MWNTs composites were dried by lyophilization.

### Characterization

Raman measurements of MWNTs and PSS/MWNTs were recorded on a Renishaw inVia with an Ar ion laser at an excitation wavelength of 633 nm. The organic contents of PSS/MWNTs composites were determined using a TGA (STA449F3, Netzsch) instrument under an

atmosphere of nitrogen at 10 °C/min from ambient temperature to 800 °C.

Near infrared spectra were tested on a FTIR (Nicolet iS10, Thermo fisher) instrument. The molecular weight of grafted PSS was measured by gel permeation chromatography (GPC, Agilent) in distilled water vs polyethylene oxide (PEO).

Brine stability testing of poly (styrene sulfonate)-wrapped MWNTs composite at room temperature

API brines was comprised by sodium chloride (8 wt%) and calcium chloride (2 wt%). The dispersion concentration of PSS/MWNTs for colloidal stability test was 4 mg/ml. The dispersion with virus salinity was sealed in glass bottles. The colloidal stability in API brine and different salinity solution was measured by visual observation, DLS measurements, and Zeta potential test at room temperature.

#### Dynamic light scattering

Hydrodynamic diameter values were measured with a Brookhaven BI-200SM instrument. Scattered light was collected with a 90° Avalanche photodiode detector, and all data were fit with the CONTIN routine. Diameters of composites solutions were measured at a concentration of ~ 4 mg/ml in various concentration of sodium chloride solution and the diameters of composites were also measured in distilled water and API brine. All measurements were made over a period of 3 min and replicated three times. Furthermore, hydrodynamic diameter of composites in distilled water could be used for comparison with the size distribution of TEM images.

#### Zeta potential

Electrophoretic mobility was measured with Brookhaven's Zeta PALS 190 Plus instrument at 15° scattering angle and 25 °C. Measurements were conducted in 10 mM KCl (Debye length  $\kappa^{-1} = 3$  nm), and zeta potential was determined with the Smoluchowski model ( $\kappa a \gg 1$ ).

#### Morphology analysis

The surface morphologies of PSS/MWNTs and aqueous dispersion of PSS/MWNTs were examined by scanning

electron microscope (SEM) (JSM-7500F, JEOL). TEM (FEI TECNAI G2 F30, Netherlands) was used to obtain the size of wrapped polymers. A dilute aqueous dispersion of PSS/MWNTs composites was deposited onto a carbon-coated copper TEM grid. An excess of nanotubes suspension was removed. Sample was used for imaging after drying at room temperature.

## Results and discussion

### Characterization

#### Raman spectra

Multi-walled carbon nanotubes (MWNTs) are based on concentric graphene sheets rolled in a cylindrical shape, and diameter of MWNTs is around tens of nanometers (Antunes et al. 2006). Therefore, the essential and useful information about the covalent attachment of the organics or polymer onto the surface of MWNTs can be obtained from Raman spectroscopy (He et al. 2009). In the first-order Raman spectra of MWNTs, prominent bands are about 1330–1380  $\text{cm}^{-1}$  (D-band) and 1400–1600  $\text{cm}^{-1}$  (G-band) (Rosca et al. 2005). As seen in Raman spectra from Fig. 2, D band at 1350  $\text{cm}^{-1}$  and the G band at 1580  $\text{cm}^{-1}$  are the characteristic peaks of MWNTs (Alam et al. 2016). After functionalization, the G band of PSS/MWNTs is slightly upshifted to 1605  $\text{cm}^{-1}$ . The  $\pi$ - $\pi$  conjugation between the sodium 4-styrenesulfonate and sidewall of MWNTs increase

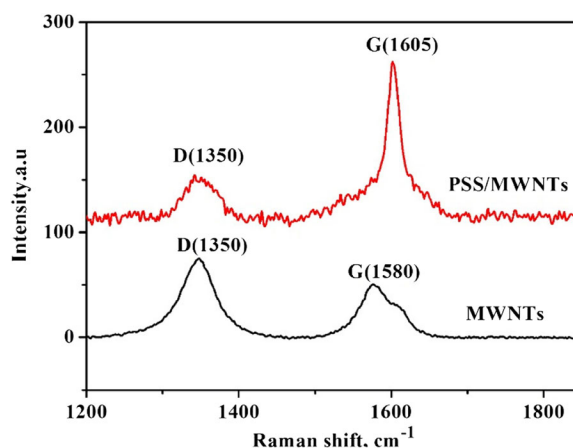


Fig. 2 Raman spectroscopy of MWNTs and PSS/MWNTs

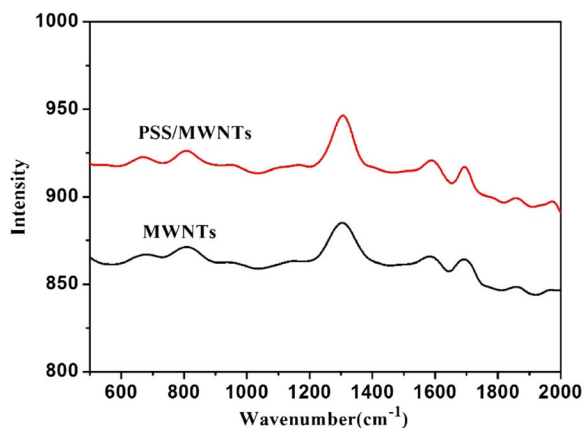
the energy necessary for vibrations to occur, which is reflected in the higher frequency of Raman peaks. It is illustrated that covalent modification of MWNTs occurred and  $\pi$ -electron network of carbon nanotubes were altered (Liu et al. 2003). It was deemed that PSS was grafted on MWNTs according covalently wrapping (Sinani et al. 2005). Sodium 4-styrenesulfonate-coated surface of MWNTs by  $\pi$ - $\pi$  interaction firstly, then free radical polymerization occurred and thus poly (sodium 4-styrenesulfonate) chains were tightly wrapped around the surface of MWNTs.

### Near-IR spectra

Absorption bands at the range of 800–1600 nm represented the van Hove transitions of semiconducting MWNTs (Elim et al. 2016). After functionalization with PSS, the near-IR spectra of PSS/MWNTs showed more sharp features than the spectrum of pristine MWNTs (Fig. 3). It indicated that some alteration caused by  $\pi$ - $\pi$  conjugation. Based on Raman spectroscopy and near-IR spectra, PSS/MWNTs composites were confirmed to be synthesized by covalently wrapping. Furthermore, small alteration in near-IR spectra showed the electronic conductivity of the MWNTs/PSS was retained after modification (Mol Menamparambath et al. 2013; Shuhui Qin et al. 2004).

### Thermogravimetric analysis

Thermogravimetric analysis (TGA) is a complementary technique that reveals grafting ratio of PSS/MWNTs composites and changes in thermal stability

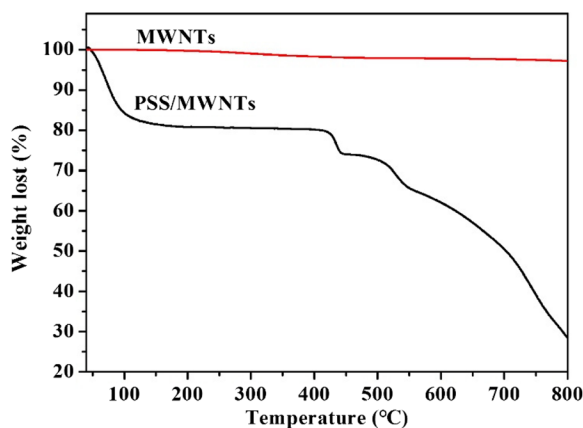


**Fig. 3** Near-IR spectra of PSS/MWNTs and pristine MWNTs

of PSS/MWNTs (Shen et al. 2008). As presented in Fig. 4, raw MWNTs itself was thermally stable with few mass loss, whereas PSS/MWNTs started to lose mass upon heating even below 100 °C, which was attributed to the water molecular encapsulated in polymer chains. From the TGA curve of PSS/MWNTs, the weight loss of PSS/MWNTs composites in the region of 400 °C to 750 °C was also observed in TGA thermograms, which was attributed to decomposition of the coated polymers on the MWNTs. And the mass loss fraction of organic content is about 38.75%. Based on the TGA measurements, grafting densities of poly (sodium 4-styrenesulfonate) for PSS/MWNTs composites were considered as 38.75%. After functionalization, a large percent of anionic polymers was covalently wrapped on MWNTs surface.

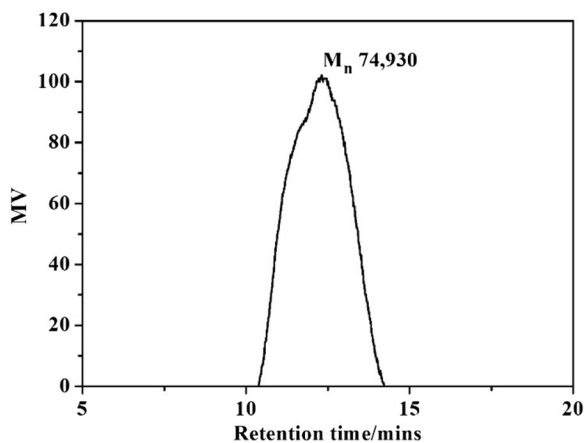
### Gel permeation chromatography

Gel permeation chromatography (GPC) was used to determine average molecular weight and the distribution of grafted poly (sodium 4-styrenesulfonate) (PSS) was displayed in Fig. 5. The number-average molecular ( $M_n$ ) of grafted polymers (PSS) was calculated to be 70 kDa. And the degree of polymerization (DOP) is about 976. The polydispersity of grafted polymer is 2.68, which indicated that the grafted PSS had a wide molecular distribution. We attributed the wide molecular distribution to the addition of multi-walled nanotubes. The defective degree of each nanotube surface was different, leading to different degree of polymerization for grafted PSS. The higher molecular weight of the PSS, the more



**Fig. 4** TGA thermograms of pristine MWNTs and PSS/MWNTs





**Fig. 5** Gel permeation chromatography of PSS/MWNTs composite

negative charges would be existed on the surface of multi-walled carbon nanotubes and the greater electrostatic repulsion was obtained. Thus, high molecular weight of grafted PSS on MWNTs was necessary.

#### Colloid stability in brines

Preliminary stability testing was performed on visual investigation. As seen from Fig. 6, the dispersions kept uniformly dark color at the concentrations of sodium chloride below the salinity of 15 wt% NaCl, including 15 wt%.

Beyond the salinity of 15 wt% NaCl, the dispersion became unstable. As shown in fig. S1, PSS/MWNTs dispersions in salinity of 16 wt% NaCl and 17 wt% NaCl were aggregated in 30mins. It indicated that the aqueous dispersion of PSS/MWNTs composite could be stable against coalescence or settling in salinity below 15 wt%. PSS/MWNTs composite also could stable in API brines (8 wt% NaCl + 2 wt% CaCl<sub>2</sub>). Base on visual inspection, PSS/MWNTs composite dispersion exhibit long-term stability in high concentrated brines and API brines. It has a significant effect on MWNTs in practical application for oil and gas industrial.

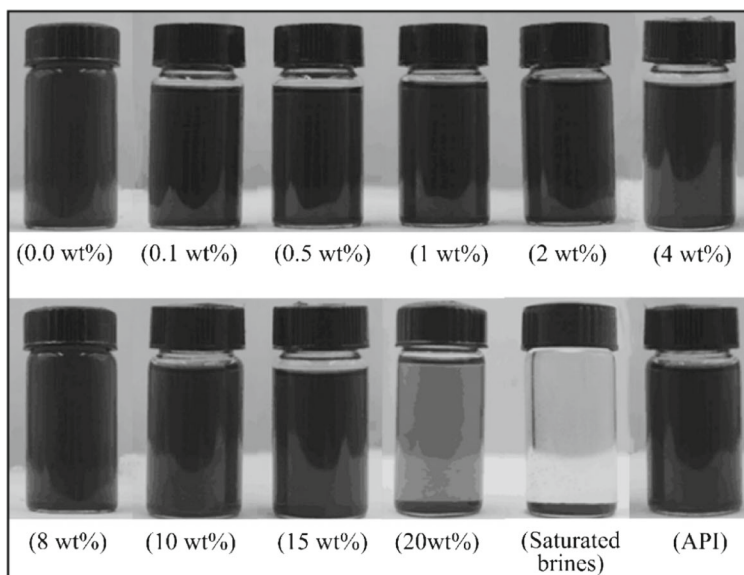
Further confirmation of the stability of PSS/MWNTs composites in various salinity brines, hydrodynamic diameter changes were obtained by dynamic light scattering (DLS) at room temperature (Fig. 7). Based on the DLS results, the average hydrodynamic diameter of PSS/MWNTs in different concentrations of brines was found to be relatively stable. Due to the presence of sulfonic group, PSS was easily solvated and the polymer chains extended in brines, which provide steric

repulsion for stabilizing the MWNTs. Furthermore, as anionic polyelectrolytes, PSS could ionize in aqueous solution, possessing lots of anionic charge that provided sufficient electrostatic repulsion for PSS/MWNTs dispersed in brines. When suspension stabled in 14 days, the average hydrodynamic diameter of composite dispersions fluctuated between  $\sim 545 \pm 110$  nm varied with salinity. After standing for 30 days, average hydrodynamic diameter of dispersions increased, and the average hydrodynamic diameters fluctuated between  $\sim 673 \pm 171$  nm varied with salinity. The average hydrodynamic diameter of PSS/MWNTs was increased with the extension of the settling time. This phenomenon may be due to the slight entanglement of the polymer chains increasing along with the time.

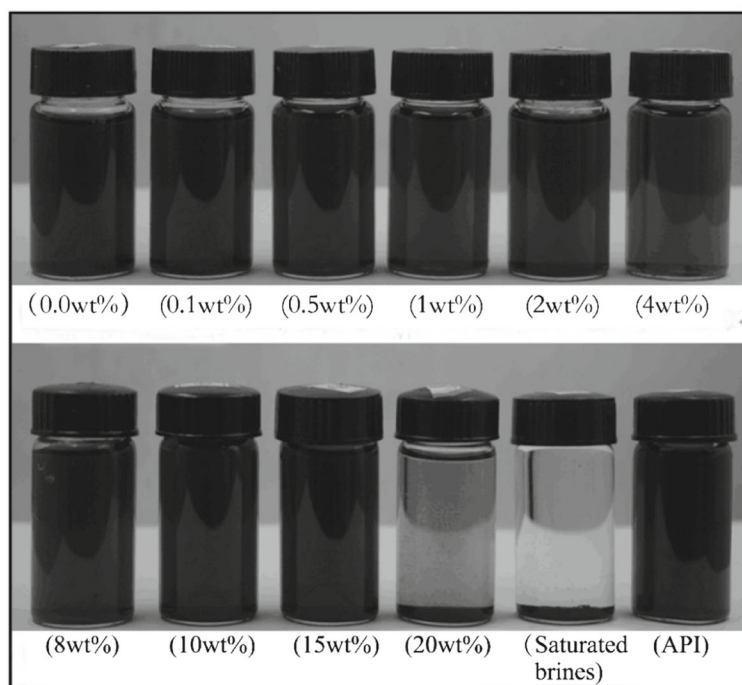
And with increasing of salinity, the average hydrodynamic diameters of dispersions showed a small increase. That was inferred that heavy ions would screen the charge of polymer chains and weaken the electrostatic repulsion among polymer chains, thus slight increase of average hydrodynamic diameters occurred. However, average hydrodynamic diameters of composites kept at  $\sim 840$  nm over 30 days at the salinity of 15 wt% NaCl. PSS/MWNTs composite dispersion in API brine showed excellent stability, and hydrodynamic diameters of composite over 14 days with mean diameters of  $\sim 600$  and  $\sim 803$  nm over 30 days. According to DLS results, PSS-wrapped MWNTs exhibit the long-term stability in API brine and salinity of 15 wt% NaCl.

Zeta potential is an indicator of colloid stability. In Fig. 8, the surface charge of the PSS-wrapped multi-walled carbon nanotubes was characterized by Zeta potential measurements as a function of salinity. The values of Zeta potential of multi-walled carbon nanotube composites in brines for 14 days kept at around  $-43 \sim -52$  mV, and at the range of  $-41 \sim -43$  mV for 30 days. Most significantly, the zeta potential values in API brines kept at  $-42 \sim -44$  mV in both 14 and 30 days. That illustrated the composites could be stable in 15 wt% NaCl solutions and API brines due to the electrostatic repulsion of NPs. Owing to the presence of sulfonic groups, the surface of multi-walled carbon nanotube were covered with a large amount of negative charges. Massive negative charge of polymer chains could overcome the compression of electric double layer by electrolytes. Therefore, PSS-wrapped multi-walled carbon nanotube could stably disperse in high salinity, and the salinity reached up to 15 wt% NaCl. The Zeta potential values of the dispersion in salinity of 16 and

**Fig. 6** Photographs of PSS/MWNTs composite dispersions at different concentrations of sodium chloride brines and API Brines



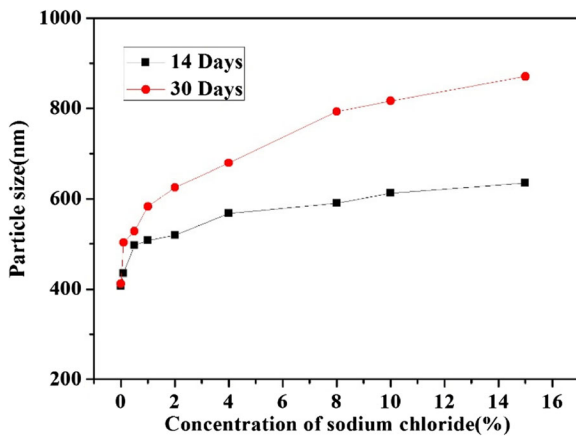
(14 days)



(30 days)

17 wt% were  $-17.96$  and  $-1.56$  mV at initial preparation, respectively (seen in Table S2). The results showed that the surface charges were less than PSS/MWNTs, and electrostatic repulsion between particles was weakened by high concentration of ion. It indicated that when the salinity was beyond 15 wt% NaCl, the stabilization

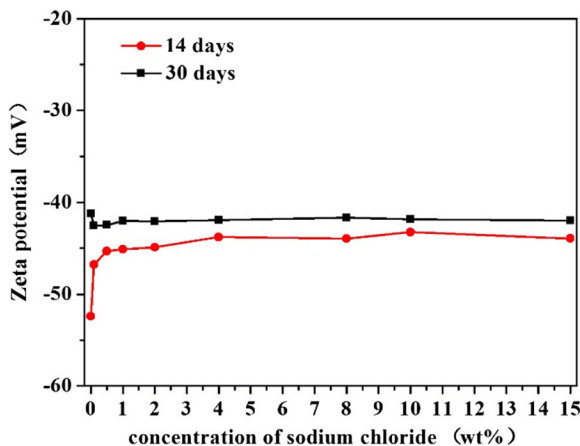
of this dispersion was broken due to the heavy concentration electrolytic iron. By contrast to zeta potential values of PSS/MWNTs stabilized in saline for 14 and 30 days, a small decrease for zeta potential values of PSS/MWNTs in 30 days was observed. It is further explained that covalently wrapping MWNTs with PSS



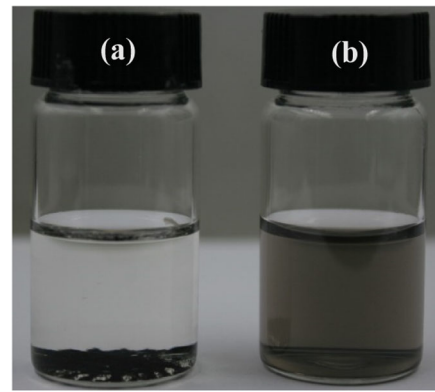
**Fig. 7** DLS data of PSS/MWNTs composites stabilized in different salinity for 14 and 30 days

can stabilize MWNTs in saline for a long time due to the electrostatic repulsion. The results were consistent with results of visual inspection in Fig. 6.

To further identify the colloid stability of grafted PSS/MWNTs in brines, a commercial poly (sodium 4-styrenesulfonate) (PSS) with high molecular weight (MW = 70 kDa) was applied for comparison test (seen in Fig. 9). Figure 9a represented the dispersion of grafted PSS/MWNTs (1 mg/ml) in 15 wt% NaCl solution, and (b) represented MWNTs suspension (0.1 mg/ml) in 15 wt% NaCl solution with 0.1 wt% PSS (MW = 70 kDa). MWNTs suspension with PSS started to aggregate in 1 h and completely settled after 24 h, whereas grafted PSS/MWNTs dispersion were kept stable in brines without any aggregation. Addition of PSS (MW = 70 kDa) in MWNTs suspension by adsorption on the MWNTs surface could not stabilize



**Fig. 8** Zeta potential of PSS/MWNTs stabilized in different concentrations of sodium chloride brines for 14 and 30 days



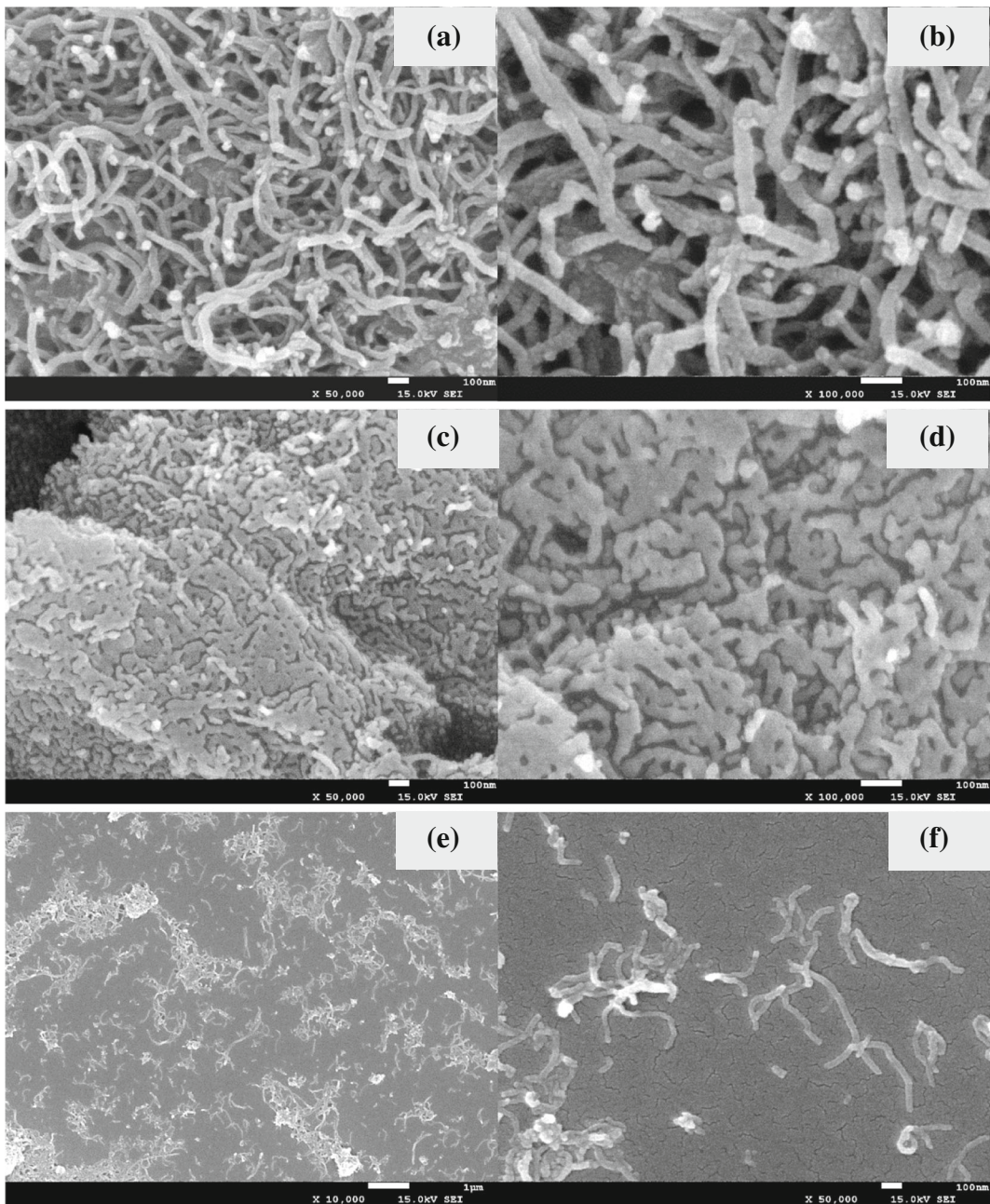
**Fig. 9** Photograph of **a** unmodified MWNTs suspension with 0.1 wt% PSS (70 kDa) in 15 wt% NaCl solution. **b** PSS/MWNTs dispersed in 15 wt% NaCl solution

the MWNTs in high electrolytes. PSS is a stabilizer to improve the stability only by physical adsorption. However, PSS/MWNTs composites were synthesized by in situ polymerization, macroradicals were capped by MWNTs bundles, then PSS chains were attached on surface of MWNTs, which helped the multi-walled nanotubes to separate from the bundles and dissolve in water spontaneously. Therefore, results of comparison test illustrated that the PSS wrapped on MWNTs by in situ polymerization was according to covalent interaction rather than physically adsorbed on surface of MWNTs indirectly.

## Morphology

Figure 10 shows SEM micrographs of as received MWNTs and MWNTs wrapped with PSS. The pristine MWNTs were presented in Fig. 10a, b, and many bundles of nanotubes were tangled. By comparison to pristine MWNTs, polymer coatings on MWNTs were obviously observed in Fig. 10c, d. That indicated poly (sodium 4-styrenesulfonate) (PSS) was successfully wrapped on the surface of MWNTs. To further confirm the state of PSS/MWNTs composites dispersed in distilled water, we investigated the aqueous dispersion of PSS/MWNTs composites by scanning electron microscope (SEM). As shown in Fig. 10e, f, nanocomposites were highly dispersed in distilled water without many tangled bundles of nanotubes. It further illustrated that attaching anionic polymers onto MWNTs could enhance the colloid stability in aqueous solution due to the electrostatic repulsion and steric repulsion.

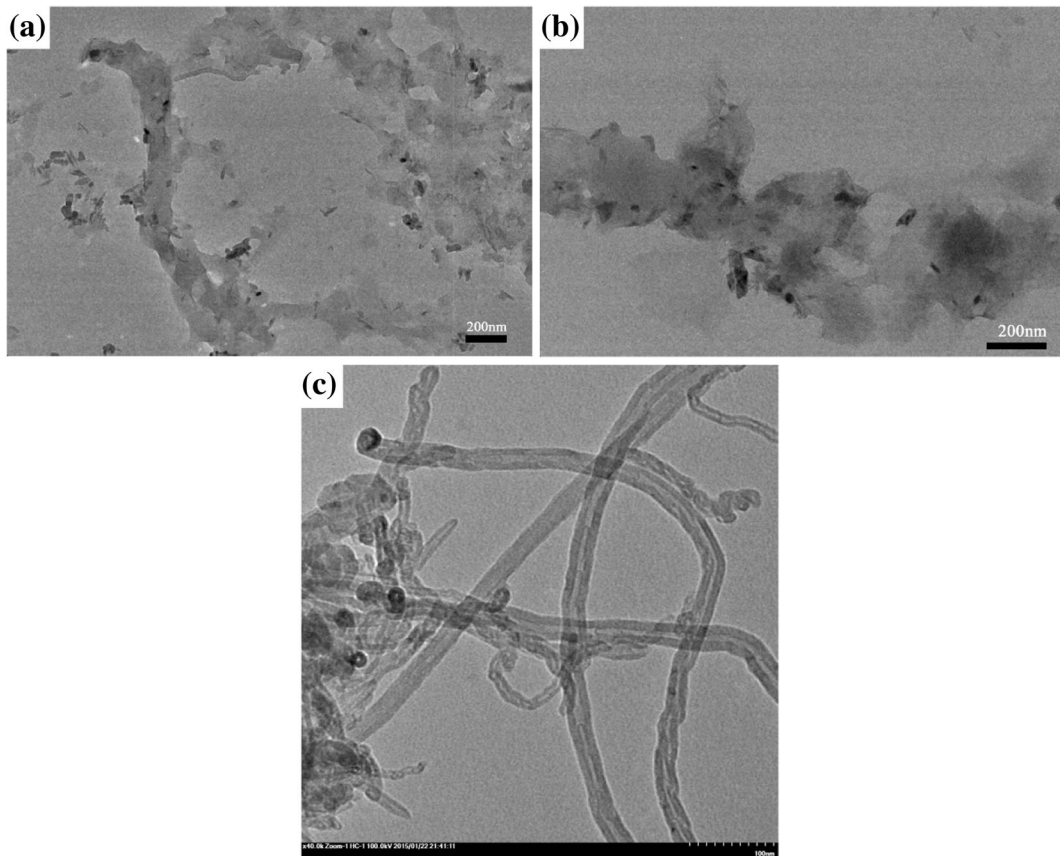




**Fig. 10** Scanning electron microscope images of as received MWNTs **a, b**, PSS/MWNTs **c, d** and PSS/MWNTs dispersed in distilled water **e, f**

Transmission electron microscopy (TEM) was used to observe the PSS/MWNTs dispersed in distilled water. As shown in Fig. 11c, the MWNTs packed into bundles that aggregate into tangled networks due to the strong van der Waals attraction. From Fig. 11a,b, MWNTs were coated by a large amount of PSS, and the thickness of polymers dispersed in distilled water was about ~

400 nm. The size of coating is in accord with hydrodynamic diameter of PSS/MWNTs dispersed in distilled water measured by dynamic light scattering (DLS). It showed that the polymer chains wrapped on multi-walled nanotubes could extend in aqueous solution. TEM images indicated that grafted polyelectrolytes (PSS) as a polymer shell, which offered both steric and



**Fig. 11** TEM images of PSS/MWNTs (a, b) and as received MWNTs (c)

electrostatic repulsion to hinder coalesce of multi-walled nanotubes and were considered to stabilize MWNTs in brines (Gerhard Fritz et al. 2002; Phenrat et al. 2008; Saleh et al. 2008).

## Conclusions

The modification of multi-walled carbon nanotubes for colloidally stable in salt solution is an essential segment for realizing the practical applications in oil and gas industry. PSS covalently wrapped on MWNTs by in situ free radical polymerization was successfully prepared, which was a simple and effective approach to improve colloid stability in salts. The PSS/MWNT nanocomposite was fully characterized by Raman, NIR, TGA, GPC, SEM, and TEM. Grafting density of PSS was estimated to be about 38.75% and the weight-average molecular ( $M_w$ ) of PSS was approximately 70 kDa. The thickness of the coated polymers (PSS) was about  $\sim 400$  nm detected by TEM images. According to visual inspection,

PSS/MWNTs nanocomposite could disperse in salt solution automatically without heavy ultrasonic and be free of aggregation over 30 days. And long-term stability of PSS/MWNTs nanocomposite dispersion in high concentrated brines was further confirmed by DLS measurements. Additionally, the zeta potential values of PSS/MWNTs composites in different salinity solution kept at around  $-43 \sim -52$  mV for 14 days, and  $-41 \sim -43$  mV for 30 days. These results showed that PSS/MWNTs composites were wrapped by large amount of anionic polymer chains and possessed sufficient negative charges. Anionic polymer chains were easily solvated and extended in salt solution, providing steric repulsion for MWNTs stabilization. Therefore, by contrast with previous work at low salinities (Wei et al. 2016), the significant stability at salinity up to 15 wt% NaCl and API brines should be attributed to the combination of the strong electrostatic repulsion rendered by the negative charges and steric repulsion provided by polymer chains. Meanwhile, anionic polymers can well stable under alkaline conditions, so the PSS/MWNTs



nanocomposites are potential materials for majority working fluids of petroleum industry.

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#### Compliance with ethical standards

**Conflict of interest** The authors declare that they have no conflict of interest.

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