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Preparation of the Core/Shell Structure of Magnetic Chitosan Particles and Application in Oilfield[1]

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Abstract—Contrary to the traditional surfactants, the novel magnetic $NiFe_2O_4$-chitosan nanoparticles have the advantage of excellent biodegradation. The $NiFe_2O_4$-chitosan nanoparticles with core-shell structure were prepared. The images of TEM and the SEM exhibited that the cubic-shape magnetic $NiFe_2O_4$ particles were encapsulated in the spherical chitosan nanoparticles. Sizes of all $NiFe_2O_4$ -chitosan nanoparticles were below 100 nm. The saturated magnetization of $NiFe_2O_4$-chitosan nanoparticles could reach 75 emu/g and demonstrated the characteristics of superparamagnetism. Evaluation of the interfacial properties of the product indicated that the interfacial tension between crude oil and water could be reduce to ultra-low values (10^{-3} mN/m) upon the magnetic $NiFe_2O_4$-chitosan nanoparticles application in several blocks in Shengli Oilfield without other additives. The magnetic $NiFe_2O_4$-chitosan nanoparticles had good salt-resisting capacity.

Keywords: magnetic nanoparticles, surfactants, superparamagnetism, interfacial tension, enhanced oil recovery

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INTRODUCTION

With the rapid development of nanotechnology, magnetic nanoparticles [1] and superparamagnetic iron oxide nanoparticles in particular have been studied in various fields of application including physics [2], medicine [3], biology [4], and materials science [5, 6]. However, the nanoparticles tend to aggregate due to strong magnetic dipole–dipole attractions [7]. Such nanoparticles are characterized by low level of anti-acid [8], anti-alkali [9], and anti-salt [10] capacities. Surfactants play an important role in adsorption of oil for enhanced oil recovery [11–13].

Due to the presence of the hydroxyl and amino groups in its structure chitosan can be chemically modified for further use as a separation media. Yang-Chuang Chang and co-workers had prepared carboxymethylated magnetic particles by carboxymethylation of chitosan and bound onto Fe_3O_4 nanoparticles via carbodiimide activation. The carboxymethylated chitosan-conjugated Fe_3O_4 nanoparticles exhibited their efficiency as anionic magnetic nano-adsorbent for removal of acid dyes and heavy metals ions. In the current study we used chitosan as an effective stabilizing agent for $NiFe_2O_4$ nanoparticles and tested their ability to reduce the oil-water interfacial tension.

The magnetic $NiFe_2O_4$-chitosan nanoparticles were obtained using $NiFe_2O_4$ as a core and chitosan as a polymeric shell. The size, structure and magnetic properties of the prepared magnetic nanoparticles were studied by TEM, SEM, XRD, and vibrating sample magnetization methods. Binding of chitosan to the magnetic nanoparticles was confirmed by FT-IR spectrophotometry.

EXPERIMENTAL

Reagents. All reagent grade chemicals were purchased from Kemel chemical reagent Co. Ltd. and purified prior to use. Chitosan ($M_w = 1.0 \times 10^5$, 95.5%) was purchased from YuHuan Chemical Company, China. Water was deionized (electrical resistivity ≥ 18.9 MΩ cm, 25°C) and deoxygenated by boiling for 1 h.

Synthesis of magnetite. $NiFe_2O_4$ was prepared without an additional stabilizer by controlled coprecipitation. In a typical synthesis an aqueous mixture of $Ni(NO_3)_2$ and $Fe(NO_3)_3$ was placed into a three-necked flask according to the stoichiometric ratio of $NiFe_2O_4$ at of 90°C and stirred mechanically (500 rpm). NaOH

[1] The text was submitted by the authors in English.

solution (0.1 mol/L) was added to adjust pH to 11 followed by refluxing for 1 h. Upon a light black sedimentation occurring, the crystal growth proceeded for 2 h with constant stirring (200 rpm) to give a stable water-based suspension. The products were isolated from the solvent by an external magnetic field followed by dispersion in deionized water and drying in an oven at room temperature.

Preparation of magnetic chitosan nanoparticles. In accordance with mass ratio $NiFe_2O_4$: chitosan = 1: 4, 0.5 g of $NiFe_2O_4$ magnetic particles were quickly added into 40 mL (5% v/v) solution of acetic acid that contained 2 g of chitosan. The solution was placed in the ultrasonic reactor for 10 min (frequency 22 kHz, power 1000 W) to disperse chitosan and make the magnetic particles uniform. This was followed by addition of 40 mL of liquid paraffin and 10 drops of Span-80. The solution was placed in the ultrasonic reactor for 30 minutes (frequency 22 kHz, power 500 W). For activating $NiFe_2O_4$ and achieving better magnetic properties the reaction system was stored at 60° for 5 h in a water bath. The cross–linked magnetic chitosan nanoparticles were formed upon adding 2 mL of glutaraldehyde and storing at 60° for 5 h. Thus prepared nanoparticles were concentrated by centrifugation (8000 rpm for 1 h) and rinsed with ethanol and deionized water four times and freeze dried for 24 h.

Characterization of magnetic chitosan nanoparticles. X-ray power diffraction (XRD) measurements were performed using a Bruker D8 diffractometer with monochromatized CuK_α radiation (λ = 1.5426 Å), 40 kV, 30 mA. FT-IR (IRPrestige-21, Shimadzu Inc.) was used to confirm the structure of magnetic $NiFe_2O_4$-chitosan nanoparticles. Size and morphology of the magnetic chitosan nanoparticles were studied by transmission electron microscopy (H-7650, Hitachi Inc.). The sample of $NiFe_2O_4$-chitosan nanoparticles for TEM analysis was obtained by placing a drop of the nanoparticle dispersion onto a copper micro-grid and evaporation at 20°. Surface of the magnetic particles was scanned by the electron microscope (Kyky-2800, Kyky technology Co., Ltd). The elemental analysis was carried out by the elemental analyzer (Vario EL III, Elementar Inc.). Magnetic measurements were performed by a vibrating sample magnetometer (VSM, PPMS-9, Quantum Design). The sample was placed in a Teflon-coated sample holder and the mass was accurately measured.

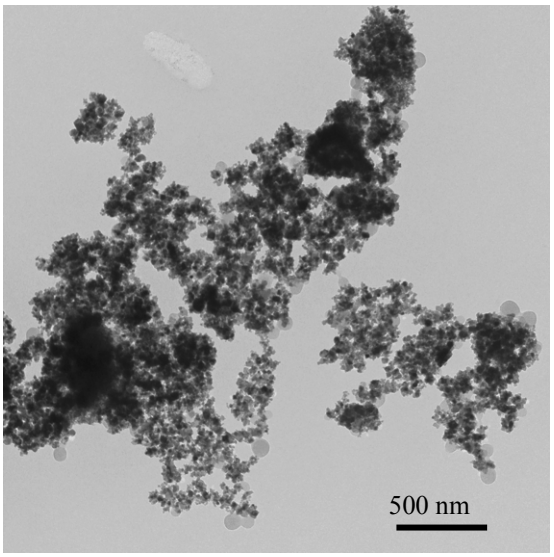

Fig. 1. TEM micrographs for the $NiFe_2O_4$-chitosan nanoparticles.

Determination of surface-activity of products. The $NiFe_2O_4$-chitosan nanoparticles were mixed with 100mL in water followed by addition of a drop of crude oil (ca. 0.1 mL) and oil-water intersurface tension measured. TX-500C full-scale automatic dynamic spinning drop interfacial tension instrument was used to measure the crude oil in GD-3, GD-4, GD-6, and GD-7 oil blocks from Shengli Oilfield, China. Unless otherwise specified, the surface activity and anti-salt performance were tested in GD-3. The products accounted for 0.4% of the injected water.

RESULTS AND DISCUSSION

FT-IR. FT-IR spectra of $NiFe_2O_4$-chitosan nanoparticles contained a band at 1635 cm^{-1} of the Schiff base which indicated that the glutaraldehyde was involved in cross-linking. The band at 528 cm^{-1} was characteristic for $NiFe_2O_4$ magnetic particles and indicated their effective crosslinking with chitosan particles.

XRD. All diffraction peaks confirmed the presence of the $NiFe_2O_4$-chitosan nanoparticles and binding of chitosan with $NiFe_2O_4$.

TEM. The TEM images of $NiFe_2O_4$ particles and $NiFe_2O_4$-chitosan nanoparticles (Fig. 1) exhibited the average diameter of the particles. The sizes of magnetic chitosan particles were below 100 nm.

SEM. According to Fig. 2 the sizes of $NiFe_2O_4$ particles were under 10 nm and had a spinel crystal

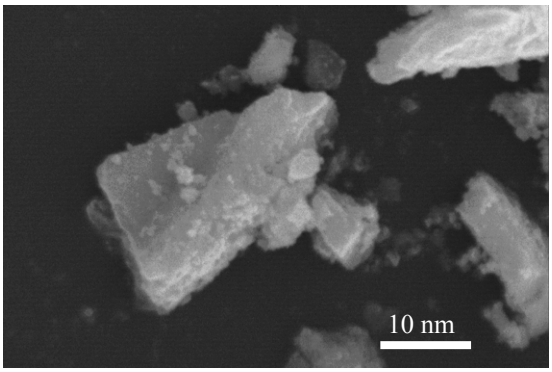

Fig. 2. SEM micrographs for the $NiFe_2O_4$ particles.

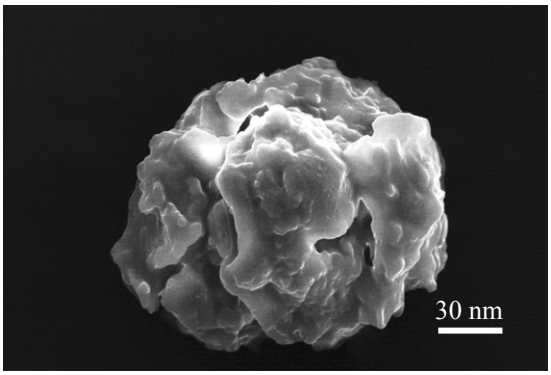

Fig. 3. SEM micrographs for the $NiFe_2O_4$-chitosan nanoparticles.

structure. Figure 3 indicated that the diameter of the magnetic chitosan particles was about 30 nm and their structure was different from that of spinel. The surface of magnetic particles was tightly wrapped and did not show $NiFe_2O_4$ particles (Fig. 3) which indicated that $NiFe_2O_4$ particles were wrapped inside the chitosan efficiently.

Elemental analysis. The elemental analysis data (C 48.13%, O 28.56%, N 4.14%, Ni 6.61%, Fe 12.56%) indicated the ratio Ni : Fe ca 1: 2 and the fact that $NiFe_2O_4$ magnetic particles were totally encapsulated by chitosan.

Magnetization test. Particles with the diameter lower than 30 nm are characterized by superparamagnetism [14]. Magnetization of pure $NiFe_2O_4$ particles was as high as 130 emu/g and that of the magnetic $NiFe_2O_4$-chitosan nanoparticles was 80 emu/g. Both kinds of particles exhibited the characteristics of superparamagnetism.

Dispersion and magnetic response properties of $NiFe_2O_4$-chitosan nanoparticles are exhibited in Fig. 4. $NiFe_2O_4$-chitosan nanoparticles had a high solubility and dispersibility in water (Fig. 4a) and would not aggregate or precipitate upon storage for one month. When subjected to a strong magnetic field, the particles would be completely separated from the solution within seconds (Fig. 4b).

Determination of surface-activity. Density of the crude oil was measured with GD-3, GD-4, GD-6, and GD-7 oil blocks (Shengli Oilfield) (0.97, 0.97, 0.89, and 0.91 g/mL respectively). Characteristics of the injected water are listed in the table.

The TX-500C full-scale automatic dynamic spinning drop interfacial tension instrument was used

(a) (b)

Fig. 4. Photographs of the $NiFe_2O_4$-chitosan nanoparticles dispersed in water: (a) without magnetic field and (b) with magnetic field.

Ions concentration and total mineralization of water in GD oil blocks

Oil block	Ions concentration, mg/L					
	Na^+	Ca^{2+}	Mg^{2+}	Cl^-	HCO_3^-	Total mineralization
GD-3	2995.8	207.2	125.9	4831.0	1437.8	9657.7
GD-4	5164.2	320.8	156.8	10564.0	480.0	16685.8
GD-6	9507.2	378.3	210.0	11186.2	599.1	21980.8
GD-7	7414.1	213.2	268.3	8757.7	819.4	17472.7

to determine the interfacial activity of the products with the oil blocks. The $NiFe_2O_4$-chitosan nanoparticles reduced the oil-water interfacial tension to less than 10^{-3} mN/m in each oil bock without any additives. The products created minimum oil-water interfacial tension of 5×10^{-4} mN/m in GD-3 and GD-4. The actual interfacial tension value was reached generally in 5 min.

Product concentration influence on oil-water interfacial tension. At $NiFe_2O_4$-chitosan concentration above 0.3 the oil-water interfacial tension reached 10^{-3} mN/m. Because salinity of the injected water from different oil blocks varied widely and it affected the oil-water interfacial tension directly, the $NiFe_2O_4$-chitosan nanoparticles must have good salt-resisting capacity. The products could reduce oil-water interfacial tension to 10^{-3} mN/m or less with NaCl concentration ~2700–16000 mg/L which indicated the products high salt-resisting capacity.

CONCLUSIONS

In summary, the novel $NiFe_2O_4$-chitosan nanoparticles were constructed with excellent core/shell structure and magnetic responsive properties. The superparamagnetic $NiFe_2O_4$-chitosan nanoparticles were able to reduce surface and interfacial tension to 10^{-3} mN/m and below without other additives. Stable oil-water interface tension could be reached in 5 min. The $NiFe_2O_4$-chitosan nanoparticles had good salt-resisting capacity.

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