Synthesis of Fe$_3$O$_4$/PAM Superparamagnetic Nanoparticles by Using Electrostatic Interaction

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Abstract. In the study, two kinds of emulsions were prepared, respectively containing nano water droplets (NWDs) with positive and negative charges on the surface. The positive charges nano water droplets, called Fe-NWDs contained Fe$^{2+}$ and Fe$^{3+}$ ions and negative charges nano water droplets, called OH-NWDs, contained OH$^-$ ions. After the above two kinds of emulsions were mixed, Fe$_3$O$_4$/PAM superparamagnetic nanoparticles (SMNPs) were synthesized in the integrated NWDs by means of electric interaction, co-precipitation and polymerization reaction. The shapes of Fe$_3$O$_4$/AM SMNPs were spherical or ellipsoid ranged in diameter from 80nm to 360nm tested by TEM and the Fe$_3$O$_4$/AM SMNPs had superparamagnetic character tested by VSM. The magnetic saturation value of Fe$_3$O$_4$/PAM SMNPs was 27.38emu/g. The XRD graph indicated Fe$_3$O$_4$ was contained in the SMNPs. The infrared spectrum proved that Fe$_3$O$_4$ was coated by PAM exactly.

1. Introduction

Recently, functional polymeric nanoparticles have renewed interest due to their potential applications in mechanical, thermal, electrical, magnetic, and smart[1,2]. Magnetic polymeric nanoparticles are considered one of most important functional polymer nanocomposites because of their widespread applications, such as biosensors, bio-separation, site-specific drug delivery, magnetic resonance imaging, and cancer hyperthermia treatments, magnetic fluids, detection and separation in microbiology, drug delivery systems and data storage[3,4].

Magnetic polymeric nanoparticles are often made of the magnetic material coated with polymer base. The magnetic materials include iron oxide, nickel, cobalt, CoFe$_2$O$_4$, and so on. By far, there are many methods for the preparation of the magnetic polymeric nanoparticles, such as physical mixing, solution polymerization and dispersion polymerization[5,6]. But some products appear magnetic nanoparticles were unevenly dispersed and some approaches were either complicated or costly.

We have known emulsifiers can improve the stability of emulsions, and ionic surfactants can give charge to the surface of the substance they cover. Therefore, in this study, anionic and cationic surfactants were used to make nano water droplets, named NWDs, with positive charges and negative charges on the surface respectively in water-in-oil (W/O) emulsion. The positive charges nano water droplets, named Fe-NWDs contained Fe$^{2+}$ and Fe$^{3+}$ ions and negative charges nano water droplets, named OH-NWDs, contained OH$^-$ ions. By means of electrostatic interaction, the Fe-NWDs and OH-NWDs were merged together rapidly and Fe$_3$O$_4$ nanoparticles were synthesized in the integrated NWDs by means of co-precipitation reaction. After polymerization, Fe$_3$O$_4$/PAM superparamagnetic...
nanoparticles (SMNPs) were synthesized in the NWDs. The measurement results of the SMNPs was discussed in the paper.

2. Experiment section

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2.1. Preparation of Fe₃O₄/PAM SMNPs

Experimental drugs included FeCl₂·4H₂O, Op10, toluene, acrylamide (AM), NH₄OH, hexadecyl trimethyl ammonium bromide (CTAB), Span80, sodium dodecyl sulfate (SDS), potassium peroxodisulfate (KPS) and FeCl₃·6H₂O. All the above chemical raw materials were of analytical grade. At 25°C, the aqueous solution, composed of 1M 2.5ml FeCl₂ and 1M 5.0ml FeCl₃, 1.85g AM, 0.30g Op10 and 0.0477g (1.309*10⁻⁴mol) CTAB dissolved in isoamyl alcohol, was slowly added to the oil solution, including 2.0g Span80 and 24ml toluene. After stirring at 2000 rpm for 2 h, the emulsion, named C-E, was formed. Similarly, aqueous solution, composed of 4ml NH₄OH, 1.85g AM, 0.20g Op10 and 0.0378g (1.309*10⁻⁴mol) SDS was slowly added to the oil solution including 2.0g Span80 and 24ml toluene. After stirring at 2000 rpm for 2 h, the emulsion, named S-E, was formed. Then the C-E was slowly added to the S-E when the stirring speed was maintained at 1000 rpm. Based on electrostatic interaction and the coprecipitation, the Fe₃O₄ magnetic nanoparticles were prepared in the black emulsion, named CS-E. After 2h, the CS-E was heated to 50°C and injected into with nitrogen for 20 min. The polymerization was initiated by adding 0.04g KPS in the CS-E. After 4 h, PAM was obtained. Now the Fe₃O₄/PAM SMNPs were synthesized. The mass ratio of Fe₃O₄ to PAM was about 20.78% in Fe₃O₄/PAM SMNPs.

The process of synthesizing the Fe₃O₄/PAM SMNPs consists of three steps: 1. the Fe-NWDs and OH-NWDs were merged together rapidly and form the integrated NWDs, 2. in the integrated NWDs, Fe₃O₄ nanoparticles were obtained through co-precipitation reaction, 3. and then Fe₃O₄/PAM SMNPs were obtained using polymerization. In the first step, electrostatic attraction was the core idea for the efficient and rapid synthesis of Fe₃O₄ nanoparticles, and this step was also the key step for the synthesis of Fe₃O₄/PAM SMNPs. The synthesis mechanism of Fe₃O₄/PAM SMNPs was shown in figure 1.

![Figure 1. Synthesis mechanism of Fe₃O₄/PAM SMNPs](image)

With stirring 2000 rpm, a lot of NWDs as micro-reactors were obtained in the C-E and S-E respectively. In the C-E, many polar groups of CTAB, Span80 and Op10 molecules adhering the surface of Fe-NWD in which Fe²⁺ and Fe³⁺ ions were scattered, shown in figure 1(a). Therefore, the Fe-NWD surface was likely to be positively charged. Similarly, in the S-E, many polar groups of SDS,
Span80 and Op10 molecules adhering the surface of OH-NWD in which OH ions were scattered, shown in figure 1(b). The surface of OH-NWD was likely to be negatively charged. When the C-E was slowly dropped into the S-E showed in figure 1(a) and (b), the Fe-NWD would collides with OH-NWD under the stirring of 1000 rpm. It can be seen from figure 1(c) and (d) that, once OH-NWD and Fe-NWD collided continuously, they would be voluntarily and rapidly merged together under electrostatic attraction. Soon the integrated NWD, in which OH-, Fe\(^{2+}\) and Fe\(^{3+}\) ions were blended, were formed in figure 1(d). After coprecipitation, the Fe\(_3\)O\(_4\) nanoparticles were immediately obtained in the integrated NWD shown in figure 1(e).

Figure 1(f) showed the polymerization was initiated by adding KPS and PAM was formed in which Fe\(_3\)O\(_4\) particles were scattered. Now Fe\(_3\)O\(_4\)/PAM SMNPs were obtained.

In addition, the stabilized emulsion system was very important for synthesis of Fe\(_3\)O\(_4\)/PAM SMNPs. The emulsion system was very stable when the hydrophile lyophile balance, named HLB, was around 5.76 [7]. The HLB values of compound emulsifiers were calculated with the following formula [8, 9]:

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HLB = \frac{\sum (HLB \times m_i)}{\sum m_i}.
\]

So the HLB of the S-E emulsion including 0.0378g SDS (HLB=40), 2.0g Span80 (HLB=4.3) and 0.20g Op10 (HLB=13.9) was about 5.76. Similarly, the HLB of the C-E emulsion including 0.0477g CTAB (HLB=15.8), 2.0g Span80 and 0.30g Op10 was about 5.76. The S-E or C-E were very stable.

2.2. Analytical methods

The photograph of Fe\(_3\)O\(_4\)/PAM SMNPs was obtained by TEM (Hitachi H-600-II, Japan). The magnetic hysteresis loops of samples were tested by a VSM (Lake Shore 7410, USA). Using KBr wafer, IR was tested by a Spectrum400 FT-IR spectrometer (PerkinElmer, USA). The XRD of Fe\(_3\)O\(_4\)/PAM SMNPs was measured by a X-ray diffractometer using Cu K\(\alpha\) radiation (\(\lambda=1.54056\ \text{Å}\)) (D8 Discover, Bruker, Germany).

3. Results and discussions

3.1. XRD results:

The XRD graph of sample was shown in figure 2. The strong peaks in the pattern could be indexed to be the (220), (311), (400), (422), (440), and (511) crystal face in the cubic Fe\(_3\)O\(_4\) (19-0629). It can be sure that the SMNPs consist of Fe\(_3\)O\(_4\).

3.2. FT-IR results:

Figure 3 showed the FT-IR spectrum of sample. The peak at 3376cm\(^{-1}\) and 3193cm\(^{-1}\) were due to N-H stretching vibration. The antisymmetric and symmetric vibrations at 2923cm\(^{-1}\) and 2853cm\(^{-1}\),

\[
\text{Figure 2. The XRD graph of sample.}
\]
respectively, were clearly observed due to the aliphatic alkyl chains. The peak at 1664 cm\(^{-1}\), 1412 cm\(^{-1}\) and 1112 cm\(^{-1}\) were due to C=O stretching vibration, C-N stretching vibration and O-C-O stretching vibration respectively. The peak at about 588 cm\(^{-1}\) was assigned to the Fe-O bonds. The spectrum of sample proved that Fe\(_3\)O\(_4\) was coated by PAM exactly.

![FT-IR spectrum of sample](image)

**Figure 3.** FT-IR spectrum of sample.

### 3.3. TEM and particle size distributions results:

Figure 4 was the TEM photo of sample respectively. The photo showed that the particles had good dispersion and ranged in diameter from 80 nm to 360 nm. The shapes of particles were spherical or ellipsoid. It was confirmed that Fe\(_3\)O\(_4\)/PAM SMNPs were synthesized in the CS-E.

![TEM photo of sample](image)

**Figure 4.** TEM photo of sample.

### 3.4. Magnetic properties:

The magnetic properties of Fe\(_3\)O\(_4\)/PAM SMNPs and Fe\(_3\)O\(_4\) were studied at 25°C in figure 5. In the absence of a magnetic field, the magnetic hysteresis loops demonstrated that the Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)/PAM SMNPs had no obvious remanence or coercivity. It just revealed that Fe\(_3\)O\(_4\)/PAM SMNPs have superparamagnetic character. The magnetic saturation values of Fe\(_3\)O\(_4\) and Fe\(_3\)O\(_4\)/PAM SMNPs were 58.10 and 27.38 emu/g respectively. The magnetic saturation value of the latter was 47.13% of the former.
Figure 5. Magnetization graphs of Fe$_3$O$_4$/PAM SMNPs and Fe$_3$O$_4$.

4. Conclusions
Using the electrostatic interaction, Fe-NWDs and OH-NWDs merged quickly and efficiently and the integrated NWDs were formed. In the integrated NWDs, the coprecipitation reaction formed Fe$_3$O$_4$ nanoparticles and the polymerization formed Fe$_3$O$_4$/PAM SMNPs. The XRD graph indicated Fe$_3$O$_4$ was synthesized in the SMNPs. The FT-IR spectrum proved that Fe$_3$O$_4$ was coated by PAM exactly. The shapes of Fe$_3$O$_4$/AM SMNPs were spherical or ellipsoid ranged in diameter from 80nm to 360nm. The Fe$_3$O$_4$/PAM SMNPs had superparamagnetic property. The magnetic saturation value was 27.38emu/g.

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