Preparation of Poly(St-HEA)/Fe₃O₄ Using a Novel Phase Inversion Method and Characterization

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ABSTRACT: Poly(St-HEA)/Fe₃O₄ microspheres with hydroxy group on the surface were prepared via phase inversion method. The morphology, composition, crystalline structure of the magnetic microspheres were characterized by transmission electron microscopy, X-ray diffraction, Fourier transform infrared spectroscopy, respectively. The effect of amount of KH-570 on modified Fe₃O₄ nanoparticles in monomer dispersity was studied. FTIR analysis shows that KH-570 was successfully introduced on the surface of Fe₃O₄ nanoparticles. XRD analysis shows that KH-570-modified Fe₃O₄ nanoparticles and poly(St-HEA)/Fe₃O₄ microspheres possesses the same spinel structure of Fe₃O₄ nanoparticles. TEM analysis shows that Fe₃O₄ nanoparticles were encapsulated into the poly(St-HEA)/Fe₃O₄ microspheres. The microspheres possesses excellent magnetic responsibility.

KEYWORDS: Phase inversion; Poly(St-HEA)/Fe₃O₄ microspheres; KH-570.

1 INSTRUCTIONS

In recent years, the preparation of magnetic composite microspheres has attracted scholars’ widely attention. The functional composite microspheres have been intensively pursued for biomedical and waste water treatment application, such as magnetic separation, protein adsorption, drug delivery and catalyst carrier. Magnetic composite microsphere has the following characteristics: (1) the surface effect and volume effect: due to the microspheres particle size is very small, the ratio of surface area to volume increases dramatically, so its surface energy greatly increase and the magnetic composite microspheres has high surface activity. (2) super paramagnetic properties: because of the addition of magnetic materials, superparamagnetism also was successfully introduced to the polymer composite microspheres. (3) functional group characteristics: Some magnetic composite microspheres have a variety of active functional groups, such as -OH, -COOH, -CHO, -NH₂, can connect bioactive substances, such as immune proteins, enzymes, etc.

There are many methods have been introduced to prepare magnetic composite microspheres including the emulsion polymerization, dispersion polymerization, suspension polymerization. The ideal magnetic composite microspheres with narrow particle size distribution, superparamagnetism, high magnetic content, etc. As a goal, this experiment adopts a novel phase inversion method to prepare magnetic polymer composite microspheres.

In this paper, we adopt phase inversion method to prepare magnetic poly(St-HEA)/Fe₃O₄ microspheres with functional groups on the surface and high magnetic content. First, Fe₃O₄ nanoparticles were synthesized through the co-precipitation of iron oxide in alkaline solution, afterward KH-570 was used to modify the surface of Fe₃O₄ nanoparticles.
Then, the magnetic microspheres of poly(St-HEA)/Fe₃O₄ were successfully synthesized by phase inversion method and magnetic nanoparticles were encapsulated in microspheres. The effect of amount of KH-570 on dispersity of modified Fe₃O₄ nanoparticles in monomers also was discussed.

2 EXPERIMENTAL

2.1 Materials

Styrene(St), 2-Hydroxyethyl acrylate(HEA), OP-10, Span-80, ethyl alcohol absolute(EtOH), glacial acetic were purchased from Tianjin Yongda Chemical Co., LTD. Azobisisobutyronitrile (AIBN), ferric chloride (FeCl₃·6H₂O), ferrous chloride (FeCl₂·4H₂O), sodium hydroxide (NaOH) were obtained from Tianjin Damao Chemical Reagent Plant. Tween-80, sodium dodecyl sulfate (SDS) were obtained from Tianjin Bodi Chemical Co., LTD. Stearyl alcohol was obtained from Tianjin Beichen Huamao Chemical Reagent Plant. KH-570 was purchased from Nanjing Aocheng Chemical Co., LTD. All the above chemical reagents were analytical grade and used without further purification.

2.2 Synthesis of Fe₃O₄ nanoparticles

Fe₃O₄ nanoparticles were prepared by co-precipitation of ferric ions and ferrous ions. 2.7g FeCl₃·6H₂O and 1.2g FeCl₂·4H₂O dissolved into 100ml deionized water were poured into a four-necked flask with a mechanical stirrer under N₂ protection and heated to 30°C for 0.5h. Then 100ml NaOH solution was added into mixture and heated for 0.5h. Eventually, the pure Fe₃O₄ magnetic nanoparticles were obtained. The black particles obtained were washed three times with water and once with absolute ethyl alcohol, and then Fe₃O₄ nanoparticles was dried in a vacuum oven at 60°C for 24h.

2.3 Preparation of KH-570-modified magnetic nanoparticles

The schematic illustration for preparation of KH-570-modified Fe₃O₄ nanoparticles was shown in Figure 1. 500ml absolute ethanol and 500ml deionized water were added into a 500ml beaker. Amount of glacial acetic was added into the mixture to adjust the pH to 4-5. 0.5g pure Fe₃O₄ nanoparticles prepared above were dispersed in mixture by ultrasonic machine using a power of 50W for 5 min. Fe₃O₄ nanoparticles were dispersed in the mixture to form a black suspension. 1.4g KH-570 was added into the black suspension under ultrasound for 5 min. The mixture was poured into a 500ml four-necked flask with a mechanical stirrer and heated to 50°C for 5h. The black magnetic nanoparticles were magnetically separated and washed 3 times with absolute ethyl alcohol. And finally KH-570-modified Fe₃O₄ nanoparticles were dried in a vacuum oven at 60°C for 24h.

2.4 Preparation of poly(St-HEA)/Fe₃O₄ composite microspheres

Amount of KH-570-modified Fe₃O₄ magnetic nanoparticles , 9ml St,3ml HEA constituted the oil phase, and 0.3g AIBN were added into a 15ml beaker. KH-570-modified Fe₃O₄ nanoparticles were dispersed in mixture by ultrasonic machine using a power of 50W for 20min. Then the black fluid was poured into 250ml three-necked flask with mechanical stirring at 70°C for half an hour. A certain amount of OP-10, Span-80 and Tween-80 as emulagor were added into above mixture with mechanical stirring at 300rpm for 15min. 0.6g SDS, 0.3g stearyl alcohol and 100ml deionized water, constituted the aqueous phase, were added into mixture with mechanical stirring at 1200rpm for 15min. Then the mixture with mechanical stirring at 250rpm for 8h keeping the temperature at 70°C. After the reaction completed, the resulting magnetic microspheres were magnetically separated. The magnetic microspheres was washed with deionized water for several times and were dried at room temperature for 24h. In the end, the powder was obtained for further characterization.

2.5 Characterization

The existence of KH-570 on the surface of Fe₃O₄ nanoparticles were examined by a Fourier transform infrared spectrophotometer (FTS-135, BIO-RAD Co., LTD, USA). These measurements were performed with pressed slice using KBr powder as diluent. Morphology of Fe₃O₄ nanoparticles, KH-570-modified Fe₃O₄ nanoparticles and the microspheres were observed under transmission electron microscope (H-7650, Hitachi Co., LTD, Japan). X-ray powder diffraction (D/MAX2500 PC, Rigaku Co., LTD, Japan) was used with Cu Kα radiation (λ = 1.54056°A).
3 RESULTS AND DISCUSSION

3.1 The effect of amount of KH-570 on modified Fe₃O₄ nanoparticles in monomer dispersity

The different amount of KH-570-modified Fe₃O₄ nanoparticles were added into styrene monomer. The light transmittance of KH-570-modified Fe₃O₄ nanoparticles in monomer was measured after 24h by visible spectrophotometer. Figure 2 shows the light transmittance of KH-570-modified Fe₃O₄ nanoparticles in monomer.

![Figure 2](image)

Figure 2. The effect of amount of KH-570 on dispersity of modified Fe₃O₄ nanoparticles in monomer.

The KH-570 modified Fe₃O₄ magnetic nanoparticles with different amount KH-570 was prepared, and their effect on monomer dispersity was investigated. As shown in Figure 2, it could be seen that the monomer light transmittance reached minimum of 59% when KH-570 content in the mixture of absolute ethanol and deionized water(volume ratio is 1:1) was 1.4g/L. It indicate that the nanoparticle dispersity in monomer reached maximum when KH-570 content in the mixture of absolute ethanol and deionized water(volume ratio is 1:1) was 1.4g/L. The decrease in dispersity as KH-570 content less than 1.4g/L was attributed to KH-570 cannot coated magnetic nanoparticles, the magnetic nanoparticles possesses strong hydrophilic. The decrease in dispersity as KH-570 content more than 1.4g/L might be due to excess KH-570 lead to flocculation. Therefore, the KH-570-modified Fe₃O₄ nanoparticles with poor dispersity. KH-570 can formed a uniform and compact molecular coated layer on the surface of Fe₃O₄ nanoparticles when KH-570 content in the mixture of absolute ethanol and deionized water(volume ratio is 1:1) was 1.4g/L. As a result, the dispersity of KH-570-modified Fe₃O₄ magnetic nanoparticles in monomer reaches optimum.

3.2 XRD analysis

X-ray diffraction patterns of pure Fe₃O₄ nanoparticles, KH-570-modified Fe₃O₄ nanoparticles and Fe₃O₄/P(St-HEA) microspheres were shown in Figure 3. According to the X-ray diffraction data cards (JCPDS, Joint Committee on Powder Diffraction Standards, No. 86-1354), the standard Fe₃O₄ crystal with spinel structure have six characteristic diffraction peaks: (2 2 0), (3 1 1), (4 0 0), (4 2 2), (5 1 1) and (4 4 0), the peaks appeared at θ = 30.58°, 35.82°, 43.66°, 54.36°, 57.32° and 63.18° agree well with the data cards. Therefore, we can conclude that pure Fe₃O₄ nanoparticles, KH-570-modified Fe₃O₄ nanoparticles and poly(St-HEA)/Fe₃O₄ microspheres possess the same spinel structure of Fe₃O₄ nanoparticles.

![Figure 3](image)

Figure 3. Powder X-ray diffraction (XRD) patterns of (a) pure Fe₃O₄ nanoparticles, (b) KH-570-modified Fe₃O₄ nanoparticles and (c) poly(St-HEA)/Fe₃O₄ microspheres.

3.3 FT-IR analysis

The FTIR pattern of KH-570-modified Fe₃O₄ nanoparticles was showed in Figure 4. It could be seen that the characteristic peak of Fe₃O₄ , around 587 cm⁻¹, which was due to the stretching vibration
of the Fe-O. The absorption peaks at 2930 cm$^{-1}$ was assignable to the stretching vibration of alkane for C-H. The absorption peaks at 1174 cm$^{-1}$ was assignable to the stretching vibration of alkane for Si-O. The new absorption peaks at 628 cm$^{-1}$ and 446 cm$^{-1}$ was assignable to the stretching vibration of Fe-O-Si and Si-O. It could be seen that KH-570 had been successfully introduced on the surface of Fe$_3$O$_4$ nanoparticles due to the appearance of the new peaks, around 628 cm$^{-1}$ and 446 cm$^{-1}$.

3.4 TEM analysis

Figure 5 shows the TEM image of magnetic composite microspheres. From the TEM image of polystyrene microspheres, it could be found that there has nearly no Fe$_3$O$_4$ nanoparticles were encapsulated into the polymer phase. However, from the TEM image of poly(St-HEA)/Fe$_3$O$_4$ microspheres, it is clear to see that Fe$_3$O$_4$ nanoparticles were successfully encapsulated into the polymer phase. The diameter of poly(St-HEA)/Fe$_3$O$_4$ microspheres were 1-2 µm. That results indicated that the poly(St-HEA)/Fe$_3$O$_4$ microspheres were successfully prepared by phase inversion method.

3.5 Magnetic responsibility analysis

Figure 6 shows the magnetic responsibility of poly(St-HEA)/Fe$_3$O$_4$ microspheres, the microspheres were uniformly dispersed into styrene monomer by ultrasonic cleaning machine. It seen that the microspheres were quickly adsorbed in the side of the permanent magnet when the permanent magnet was close to the microspheres. It indicated that the microspheres possesses excellent magnetic responsibility.

4 CONCLUSIONS

The KH-570 modified Fe$_3$O$_4$ nanoparticles with different amount KH-570 was prepared. It is clear to see that KH-570 modified Fe$_3$O$_4$ nanoparticles dispersity in monomer can reach optimum when KH-570 content was 1.4g. FTIR analysis shows that
KH-570 was successfully introduced on the surface of Fe₃O₄ nanoparticles. XRD analysis shows that KH-570-modified Fe₃O₄ nanoparticles and poly(St-HEA)/Fe₃O₄ microspheres possess the same spinel structure of Fe₃O₄ nanoparticles. TEM analysis shows that Fe₃O₄ nanoparticles were encapsulated into the poly(St-HEA)/Fe₃O₄ microspheres. The microspheres possess excellent magnetic responsibility. Therefore, the microspheres have much promising potential applications in many others fields, such as enzymes immobilization and biological separation.

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