Synthesis of nanoparticle emulsion collector HNP and its application in microfine chalcopyrite flotation

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Abstract. Hydrophobic polystyrene nanoparticles bearing thiazole groups named HNP were used as collectors to improve recovery of microfine chalcopyrite in flotation. HNP adsorbs onto microfine particles selectively, which were modified hydrophobically to induce flotation effectively. Particle size and scanning electron microscope analysis for HNP show that HNP is a spherical nano particles with small size, uniform distribution and good dispersion. Infrared spectrum analysis for HNP proved that functional monomer 2-mercapto styrene acrylic thiazole was bonded chemically onto styrene. Flotation test results indicate that HNP is the right collector of chalcopyrite. Especially, the recovery of chalcopyrite is higher than 95% in neutral and acid media. FTIR results reveal that the flotation selectivity of collector HNP is due to strong chemical absorption onto chalcopyrite surface. Zeta potential analysis shows that the zeta potential of chalcopyrite decreased more quickly after interaction with HNP with the increase of pulp pH value, confirming that collector HNP is an anionic collector. Scanning electron microscope conform that HNP has good selective adsorption on chalcopyrite.

1. Introduction
With the depletion of richer or more easily separation minerals, it is much more necessary than anytime before to utilize refractory ore, especially ultra-fine ones. Much of the undisassociated minerals outflow when treating ultra-fine particles, where the efficiency of separation is relatively low. In order to make the fine embedded ores finely liberate, it is necessary to comminute the particles less than 30 μm in diameter. However, most typical mineral processing techniques with traditional agents fail in separating the ultra-fine minerals. It is urgely to find out a new method to recover the ultra-fine ores efficiently [1-4].

A variety of reasons why fine-grained mineral is difficult to choose have been studied by mineral processing workers from different viewpoints [5-7]. The research work mainly includes four aspects: the flotation solution chemistry, the agglomeration flotation technology, flotation equipment, and flotation reagents including collector, regulator, flocculant, and frother were conducted in this paper. However, the reported methods namely carrier flotation, selective flocculation flotation and column flotation cannot be applied to industrial practice at present.

Carrier flotation can increase mineral particle size indirectly by carriers, thereby increasing its collision probability with bubbles. Due to the technological requirements of high strength of dough, strict carrier particle size and high proportion of carrier, it is difficult to implement [8, 9]. Non-selective coagulation among slurry is one of the important obstacles in fine-grained selective flocculation. Pulp dispersion in advance is dispensable before flocculation. The key point to complete
separation of minerals and gangue is to find effective flocculant and dispersant. The inevitable ion in the water could produce a great impact on the selective flocculation. Selective flocculation uses reunion between purpose mineral particles to increase mineral particle size, but gangue minerals mixed in the flocules make it difficult to obtain the high grade concentrate [10-13]. Micro-bubble flotation column can produce more small bubbles and then increase collision probability of the mineral and bubble, which has a certain effect on the recycling of micro fine particle minerals. But its large-scale application is limited by some shortcomings such as large elevation difference, complex configuration, easy block of aerator, tumble inside the cylinder of pulp, poor adaptability and stability of the minerals [14, 15].

In this article, starved-feed semi-batch emulsion polymerization was applied to synthesize nanoparticle flotation collector with functional MBT moieties which can adsorb on chalcopyrite selectively. The polymerization of styrene and MBT is shown in figure 1. Addition reaction of C=\( \text{C} \) double bond is predicted to happen in the polymerization [16-18] effect of the emulsifiers on flotation was studied.

\[ \text{HC} = \text{C} \text{H}_2 + n \text{SH} \rightarrow [\text{H} \text{C} = \text{C} \text{H}_2]_m [\text{SH}]_n \]

**Figure 1.** Polymerization reaction equation of styrene and MBT.

2. Materials and methods

2.1. Materials

**Chemicals:** Styrene (St) with analytic grade were used as monomers. Sodium dodecyl sulfate (SDS), polyethylene glycol and sodium lauryl sulfate with analytic grade were used as emulsifiers. Ammonium persulphate (APS) with analytic grade was used as initiators. 2-mercapto benzothiazole (MBT) with analytic grade were used as functional monomer that can be copolymerized into the composite particle. Styrene was purified further by vacuum distillation. water used throughout the experiment was deionized.

**Mineral:** Pure mineral purchased from Dexing copper mine had a Cu grade of 33.40%. Note that the Cu grade of 100% pure chalcopyrite is 34.56. The purity of quartz is 99.40%, and the purity is 95.96%. The minerals were ground to less than 23 \( \mu \text{m} \) with ceramic ball mill.

2.2. Synthesis of nanoparticle collector

The polystyrene-co-SDS latex was prepared by monomer-starved semi-batch emulsion polymerization. The polymerization was conducted in a three-neck flask equipped with a condenser, two rubber stoppers holding syringe needles (one for nitrogen, the other for monomer addition). The flask was heated in a water bath with magnetic stirring. 100 mL deionized water containing 0.08 g of SDS and 0.5 g of styrene were charged into the flask, followed by nitrogen purging for 30 min at 70 °C with 400 r/min stirring. 10 mL of water containing 0.025 g of APS initiator was injected into the reactor to initiate the polymerization 0.125 g of MBT, dissolved in 4.9 g of water and an additional 4.5 g of styrene were added for 5 h. The reaction was stirred at 70 °C with 400 r/min for another 19 h. The resulting latex was dialyzed for at least 5 days against deionized water, after which the dialysate conductivity was less than 20 \( \mu \text{S/cm} \) [19, 20].

2.3. Scanning electron microscope measurement

The nanoparticles and flotation concentrate were characterized by scanning electron microscope (SEM, MLA650F, FEI) to obtain the surface morphology of nanoparticles and its adsorption form on the mineral surface.
2.4. Particle size analysis
Particle size of nano latexes was measured by Malvern Zetasizer NanoZS laser particle size analyzer. 5 ml emulsion was filled in the tank with 200 ml distilled water to prepare the solution. Measurement angle is 90°, and laser source is He-Ne at a wavelength of 633 nm.

2.5. Infrared spectra measurement
The infrared spectra of the samples were measured using a ALPHA Fourier transform infrared spectrometer. Sample and KBr with the ratio of 1:100 were mixed and ground in an agate mortar. The mixture which formed a transparent sheet by a pressure mold was put on the sample holder and measured. The sample wavenumbers range was from 400 to 4000 cm⁻¹.

2.6. Flotation experiment
In a conventional flotation experiment, 2 g of chalcoprite washed by ultrasonic for 5 minutes to remove oxides on the mineral surface was added into a 35 mL effective volume microflotation cell in each test. The washing solution of samples was decanted, and the remaining part was floated for at least 3 min. Then, an appropriate amount of the synthesized HNP collector was added to the slurry while agitating at about 1500 rpm followed by a period of 3 min for slurry conditioning. At the end of conditioning, air was fed and the concentrate was collected for 6 minutes. The concentrates and tailings were filtered, dried, weighted and calculated successively for recovery.

2.7. Zeta potential measurement
Zeta potential was measured by means of ZetaProbe (Colloidal Dynamics). The pure minerals were ground to be smaller than 5 μm in the agate mortar. 2 g mineral was added to a beaker with 50 mL distilled water, then the mineral was cleaned ultrasonically for 5 min. Next, 1 ml emulsion was added into the solution, which was stirred for 3 minutes. Finally, pH of the suspension was regulated to a desired value with HCl or NaOH solution which was ready for measurement.

3. Results and discussion
3.1. Nanoparticle emulsion properties
3.1.1. Particle size and scanning electron microscope analysis for HNP. Shape and surface characteristics of the nanoparticles exert a great influence on its properties. Scanning electron microscope (figure 2) illustrates that size of the HNP is small, the particles are dispersed uniformly. Particle size distribution (figure 3) shows that the mean particle size of HNP is 77 nm, which is in agreement with the results of SEM.

![Figure 2. Scanning electron microscope for HNP.](image1)

![Figure 3. Particle size distribution for HNP.](image2)
3.1.2. Infrared spectrum analysis for HNP. Figure 4 shows the infrared spectra for the HNP. The absorptions at 3026 cm\(^{-1}\) and 698 cm\(^{-1}\) are attributed to the stretching vibration mode of —CH— and —CS— groups, respectively. The absorption at 1674 cm\(^{-1}\) which is assigned to the phenyl ring skeleton and the stretching vibration absorption at about 1600 cm\(^{-1}\), 1500 cm\(^{-1}\), 1450 cm\(^{-1}\) which are appeared in three different unsaturated —C=C— group suggest the existence of benzene ring. The absorption between 2925 and 2840 cm\(^{-1}\) are for the asymmetric stretching vibration of —CH\(_2—\) group. The absorption at 1027 cm\(^{-1}\) is stretching vibration absorption of —C=N— group. Absorption ranging from 1400 to 1430 cm\(^{-1}\) belong to NCS ring of MBT which are not observed indicates that —C=N— double bond in MBT cracks during the polymerization process. The absorption ranging from 880 to 680 cm\(^{-1}\) that change with the number and position of substituents on the phenyl ring are attributed to outside plane bending vibration of —CH— in alkene, which reveals the substituted degree and configuration on benzene ring. The above results confirm the reaction between styrene and MBT.

![Infrared spectrum of HNP](image.png)

**Figure 4.** Infrared spectrum of HNP.

3.2. Flotation test

3.2.1. HNP dosage. Tests of the dosage of HNP at natural pH (pH=6) on the flotation efficiency of chalcopyrite, pyrite, quartz respectively were conducted and results are shown in figure 5.

![Flotation efficiency](image.png)

**Figure 5.** The relation between HNP dosage and recovery ratio.
It can be seen from figure 5 that in a certain range, with the increase of the dosage of HNP, the recovery of three kinds of mineral increased gradually, and recovery of chalcopyrite and pyrite grow much faster than that of quartz. Recovery of chalcopyrite increases from 40.21% to 96.32% rapidly with increasing dosage of HNP from 0.4 ml to 1.0 ml, and it doesn’t continue to increase as the dosage of HNP goes up further. Recovery of pyrite increases from 29.87% to 66.44% with increasing dosage of HNP from 0.4 ml to 1.2 ml. Recovery of quartz increases from 9.89% to 25.88% slowly as the dosage of HNP rises up from 0.4 ml to 1.2 ml. Comparison of the recoveries among the three kinds of minerals shows that the optimum concentration with a higher chalcopyrite recovery and a lower pyrite and quartz recovery appears in the dosage of HNP of 1.0ml so that good separation of chalcopyrite can be achieved.

3.2.2. pH value condition. The pulp pH value has a substantial influence on the mineral recovery rate in the sulfide minerals flotation. When amount of HNP is 1ml, the influence of pulp pH value on microfine particle chalcopyrite flotation efficiency was shown in figure 6. The pH values were adjusted with hydrochloric acid and sodium hydroxide respectively.

![Figure 6. The influence of the pulp pH on recovery ratio.](image)

It can be seen that, with the increase of pulp pH, chalcopyrite recovery decreases slowly at first and then dropped dramatically, and pyrite recovery decreases quickly in the pulp pH value set, while quartz recovery rate rise slowly. Chalcopyrite can be well floated in acid and neutral media, and the recovery amount are bigger than 95.0% when the pulp pH≤6. Recovery of pyrite reduce from 78.82% down to 32.70% with the pulp pH increases from 2 to 10. The maximum recovery ratiof quartz is 30.69% at pH=10. Then, pH 6.0 is the best result, giving 95.02% chalcopyrite recovery, 64.86% pyrite recovery and 23.20% quartz recovery.

The above flotation test results show that without depressant and frother, HNP shows well selectivity to chalcopyrite under neutral and weak acid conditions at dosage of 1 ml.

3.3. Interaction mechanism of HNP and minerals

3.3.1. Infrared spectra of chalcopyrite before and after interaction with HNP. The absorption mode between HNP and minerals can be analyzed by comparison of infrared spectrum of chalcopyrite before and after interaction with HNP. As shown figure 7 the infrared spectra of chalcopyrite treated with HNP changed obviously s. The characteristic peaks at 3025cm⁻¹ and 697cm⁻¹ of —CH— and —CS— stretching vibration absorption, respectively and at 2921.97cm⁻¹ and 2851cm⁻¹ of —CH₃— asymmetric stretching vibration as well as at 754cm⁻¹ of —CH— bending vibration absorption of HNP
appeared. It can also be seen that the wavenumber in 1516 cm\(^{-1}\) of \(\text{C} = \text{C}\) stretching vibration absorption peak shifts to 1492 cm\(^{-1}\) leading to a 24 cm\(^{-1}\) displacement. The shift or disappear of corresponding peaks in the infrared spectra of chalcopyrite treated with HNP prove that chemical absorption occurs between HNP and chalcopyrite.

**Figure 7.** Infrared spectra of the chalcopyrite before and after interaction with HNP.

### 3.3.2. The zeta potential before and after chalcopyrite with HNP.

Zeta potentials of chalcopyrite and chalcopyrite interaction with HNP with respect to pH value are shown in figure 8. The figure shows that chalcopyrite surface zeta potential showed a downward trend along with the solution pH increases. Isoelectric point of chalcopyrite changes from 5.1 to 4.3 after been adsorbed by HNP, which shows that the nanoparticles emulsion is a kind of anionic collector because of the anionic emulsifier SDS used in emulsion synthesis. When pH value is lower than isoelectric point, mineral charges positive and zeta potential of chalcopyrite adsorbed with HNP decreases, due to the electrostatic force. When the pH value is higher than isoelectric point, mineral turned to be negative and zeta potential of chalcopyrite adsorbed with HNP still decreases, which indicates that other effects such as hydrogen bond or chemical adsorption exist.

**Figure 8.** Relationship between zeta potential of chalcopyrite and pulp pH value.
3.3.3. *Scanning electron micrographs of minerals with HNP.* SEM photos of the mineral flotation concentrates and tailing in HNP system are shown in figure 9. It can be seen that there is a large number of HNP attached in chalcopyrite concentrate while very few in chalcopyrite tailings. The HNP attached in quartz concentrate can be ignored. There are some HNP in the pyrite concentrate but less than it in chalcopyrite concentrate. This shows that HNP display well adsorption with chalcopyrite which increase its flotability. The result of adsorption capacities of HNP on chalcopyrite, pyrite and quartz is proportional to the recovery ratios in flotation.

![SEM photos of the mineral with HNP](image)

Figure 9. SEM of the mineral with HNP.

4. *Conclusions*

In summary, the HNP prepared by emulsion polymerization showed that nanoparticle flotation collectors can promote microfine chalcopyrite flotation. The specific conclusions from this work are as following:

1. Particle size and scanning electron microscope for HNP declared that during the emulsion polymerization, spherical nano particles were obtained with small size, uniform distribution and good dispersion.

2. Infrared spectrum analysis for HNP illustrated that functional monomer MBT was bonded to styrene chemically.

3. Flotation experiments showed that the HNP has well selectivity to chalcopyrite at acid and neutral media. With addition of 1 ml HNP, the recovery ratio of chalcopyrite is 96.32% at pH=6.
(4) Zeta potential experiments demonstrated that, after interaction with HNP, zeta potential values of chalcopyrite became more negative. The results indicated that the HNP belongs to anionic collector adhesive to minerals surface.

(5) Infrared spectrum demonstrates that the adsorption form of HNP onto chalcopyrite surface is chemical absorption, which result in the flotation selectivity of HNP to chalcopyrite.

(6) Scanning electron microscope confirmed that HNP has strong and selective adsorption on chalcopyrite.

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