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## Tetrahydrofurfuryl-functionalized polystyrene nanoparticles as collectors for low rank coal flotation

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**Abstract:** In this paper, tetrahydrofurfuryl-functionalized polystyrene nanoparticles (TFPNs) were evaluated as collectors in low-rank coal flotation. A series of TFPNs were prepared by immobilizing tetrahydrofurfuryl groups onto the surface of polystyrene nanoparticles (PNs), and further characterized in terms of their size, shape, surface charge and surface functionalization group concentration (SFGC). The coal flotation performance using TFPNs was compared to that using PNs and diesel oil (DO). The interaction mechanisms between TFPNs and low-rank coal were also discussed. The results show that TFPNs gave higher recovery than that given by PNs and DO. Smaller TFPNs were more effective flotation collectors. The recovery of TFPNs increased firstly and then decreased with SFGC. TFPNs can specifically deposit onto the low-rank coal particles with the hydrogen bonding function between tetrahydrofurfuryl groups and oxygen-containing functional groups, and promote low-rank coal flotation by increasing the hydrophobicity and roughness of coal particle surface with the adsorbed TFPNs. It was demonstrated that TFPNs introduced a new class of collectors for low rank coal flotation.

**Keywords:** nanoparticles, low rank coal, flotation, collectors

### 1. Introduction

In China, low-rank coal reserve is close to 5000 million tons, accounting for about 42% of total coal reserves. In recent years, with the development of mining mechanization and the deterioration of geological conditions, the content of fine low-rank coal has increased sharply. Froth flotation is an effective separation method for fine coal cleaning and upgrading that is based on the differences in the surface hydrophobicity of organic matter and mineral matter (Xing et al., 2016). However, flotation of fine low-rank coal is difficult to achieve by using conventional oily collectors due to the presence of a large quantity of surface oxygen functional groups (Shobhana, 2012; Xia et al., 2013; Liao et al., 2017; Liao et al., 2016). These groups can reduce the hydrophobicity of the coal surface because the thick hydration shell will be generated through hydrogen-bonding interaction (Xia et al., 2016; Tian et al., 2017). This thick hydration film prevents the adsorption of the collectors on the coal surface as well as the attachment of coal particles on the bubbles.

It is well known that the addition of surfactants or oxygenated functional groups to oily collectors can significantly improve the low rank coal flotation performance (Shobhana, 2012; Jena et al., 2008; Gui et al., 2017; Chander et al., 1994). Numbers of works have been conducted to investigate the interaction between low coal particles and the collectors. The most representative work was done by Jia et al. (Jia et al., 2000). They used a series of non-ionic surfactants, containing oxygenated and aromatic functional groups, i.e., tetrahydrofurfuryl esters (THF), as collectors to enhance low-rank/oxidized-coal flotation. The members of the THF series were found to be more effective collectors than the oily collectors for

both oxidized and oxidized coals. THF series would adsorb onto the oxygenated surface sites on the coal through hydrogen bonding, hydrophobic bonding of the aliphatic hydrocarbon chain with the hydrophobic sites on the coal surface and  $\pi$ -bonding of the benzene ring on the hydrocarbon chain of the collector with aromatic sites on the coal surface. It was proved that tetrahydrofurfuryl group is an efficient oxygenated functional group to anchor collectors on the polar part of low-rank coal surface through hydrogen bonding. In this study, we discussed a series of tetrahydrofurfuryl-functionalized polystyrene nanoparticles which were used as a new class of flotation collectors for low-rank coal flotation.

In materials science and nanotechnology, nanoparticles have been used to induce super-hydrophobicity or ultra-hydrophobicity. It was found that hydrophobic nanoparticles adsorbing onto solid surface could give a high contact angle (Yang, 2011). Inspired by this, Dr. Pelton's team proposed to use polymeric nanoparticles as flotation collectors (Dong, 2016). Their work involved small scale laboratory batch flotation tests, either with glass beads or with pentlandite ores (Abarca et al., 2015; Abarca et al., 2018; Dong et al., 2017). Key findings from the glass bead experiments included: surfactant-free polystyrene latex was sufficiently hydrophobic to promote glass bead or mineral flotation (Yang and Pelton, 2011); as little as 10% coverage of the glass bead surface was sufficient to give good flotation; (Yang et al., 2012) small nanoparticles (~50 nm diameter) are superior to larger (>100 nm) particles; (Yang et al., 2013) and, softer copolymers perform better than hard polystyrene (Dong et al., 2016). One of the most important findings from the pentlandite flotation was that the copolymerization of imidazole surface functional groups can promote selective nanoparticle deposition onto nickel sulfide rich surfaces (Yang et al., 2013). Besides, other groups have recently synthesized and evaluated several inorganic nanoparticle flotation collectors. Hajati et al. (Hajati et al., 2016) introduced natural hydrophobic talc nanoparticles as a collector in a flotation of quartz, and it was found that the collector dosage was affected by nanoparticle size and flotation time. Mehdi et al. (Mehdi et al., 2016) synthesized  $\text{SiO}_2\text{-TiO}_2$  hydrophobic nanocomposite as a collector for hematite flotation and this nanoparticle collector showed an improvement in both the recovery and selectivity.

In spite of the fact that several kinds of nanoparticles have been successfully used, the application of nanoparticles in coal flotation is limited. We recently have reported that a clean concentrate was obtained from floating high ash coal fines by using cationic hydrophobic polystyrene nanoparticles (PNs) as a collector (An et al., 2017). However, this investigation was conducted on easy-floating anthracite coal and the performance of such nanoparticle collector on difficult floated low-rank coal was still not known. In the present study, a series of nanoparticle flotation collectors special for low-rank coal, i.e., tetrahydrofurfuryl-functionalized polystyrene nanoparticles (TFPNs), were prepared by emulsion polymerization, in which hydrophobic PNs were functionalized with Tetrahydrofurfuryl Methacrylate. The flotation performance using TFPNs was compared to that using PNs and diesel oil (DO). The effect of several parameters such as surface functionalization group concentration (SFGC), nanoparticle size and dosage on the low-rank coal flotation performance was investigated. The interaction mechanism between TFPNs and low-rank coal surface was also discussed.

## 2. Experimental

### 2.1. Materials

#### 2.1.1. Coal sample

A gravity concentrate coal sample was collected from Daliuta mine, Shaanxi Province, China. The sample was ground first in a jaw crusher and then in a laboratory type ball mill (porcelain) and screened to -0.5mm (-74 $\mu\text{m}$  accounting for 90%). The proximate analysis of the coal was as follows:  $A_{\text{ad}}=3.59\%$ ,  $M_{\text{ad}}=8.52\%$ ,  $V_{\text{ad}}=33.26\%$ ,  $S_{\text{d}}=0.16\%$ , where  $M_{\text{ad}}$  is the moisture content,  $A_{\text{ad}}$  is the ash content,  $V_{\text{ad}}$  is the volatile matter content, and  $S_{\text{d}}$  is the sulfur content.

X-ray diffraction (XRD, D8 ADVANCE, Bruker, Germany) was used to gain the coal phase composition. XRD analysis of the coal samples is shown in Fig. 1. Kaolinite and Quartz are the main mineral impurities. X-ray photoelectron spectroscopy (XPS, ESCALAB 250Xi, Thermo Scientific, Waltham, MA, USA) experiments was conducted to obtain more information regarding the coal surface properties. Fig. 2 shows the XPS C 1s fitting spectra of the coal sample. The peak fitting was done by

CasaXPS software and the binding energy was calibrated by setting the C1s hydrocarbon peak to 284.8 eV. The spectra were fitted with four Gaussian-shaped peaks that occur at 284.8, 285.3, 286.3 and 289.1 eV to calculate the groups contents of C-C and C-H, C-O, C=O, and O=C-O. The relative contents of carbon forms of the coal samples have been listed in Table 1. The content of C-O, C=O, and O=C-O was 17.79%, 2.12% and 5.05%, respectively. Although the content of C-C and C-H groups is the highest, there is still a large amount of oxygen-containing functional groups (C-O, C=O, and O=C-O) on the coal surface that increase the hydrophilicity of the coal samples.

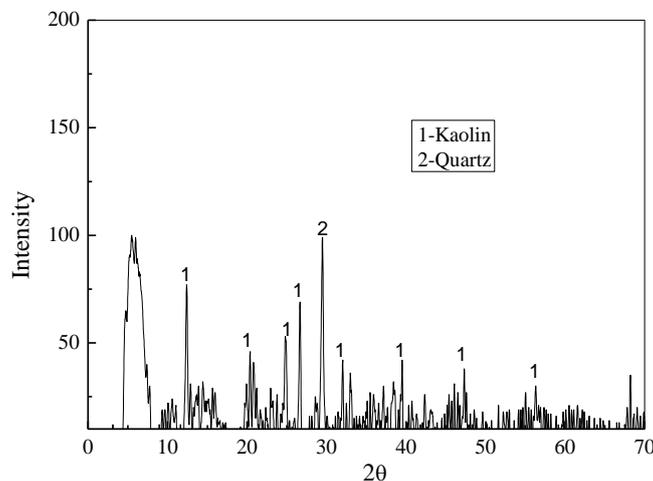


Fig. 1. XRD analysis of the coal sample

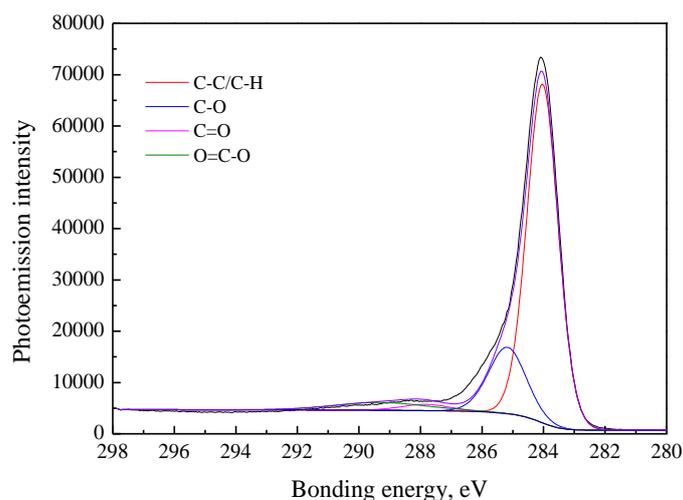


Fig. 2. The XPS C 1s fitting spectra of coal sample

Table 1. The relative contents of carbon forms of coal sample

Types	C-C/C-H	C-O	C=O	O=C-O
Contents (%)	75.04	17.79	2.12	5.05

### 2.1.2. Reagents

Styrene (St, 99%) was purchased from LingFeng. Cetyltrimethylammonium bromide (CTAB, 99%) and 2,2'-azobis (2-methylpropionamide) dihydrochloride (V50, 99%) were purchased from Sinopharm and used as supplied. Divinylbenzene (DVB, 55%) and Tetrahydrofurfuryl Methacrylate (THFMA, >97%) was purchased from Aladdin and removed the inhibitor with sodium hydroxide solution (55%) before use.

## 2.2. Nanoparticle Preparation and characterization

### 2.2.1. Nanoparticle preparation

A series of cationic poly (St-CTAB-THFMA) were prepared by surfactant emulsion polymerization, as shown in Fig. 3. The polymerization was conducted in a three-necked flask equipped with a condenser, two rubber stoppers holding syringe needles, and a magnetic stirring bar. First of all, 130 ml of deionized water was charged to the reactor followed by 2.73 g of St, 0.31 g of DVB, certain CTAB and THFMA. Then, the mixture in the reactor was equilibrated for 2 h with a stirring speed of 350 rpm, after which the temperature was raised up to 75 °C under nitrogen. The mixture reacted for 30 minutes before 0.10 g of V50 dissolved in 10 mL of water was injected to initiate the polymerization. Finally, the reaction was stirred at 75 °C for 7 h. The resulting latex was dialyzed for 1 week against deionized water with changing the water every 12 h before further characterization or use in flotation test.

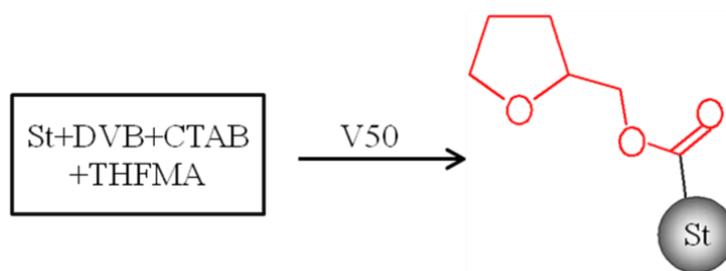


Fig. 3. Polymerization principle of the TFPNs

### 2.2.2. Characterization

The zeta potential and diameter of the nanoparticles were determined using a ZetaPALS instrument (Brookhaven Instruments Co., USA). Before measurement, the freshly prepared nanoparticles were appropriately diluted. All measurements were performed at room temperature after equilibration for 10 min. The data were obtained with the average of three measurements.

The morphology of the nanoparticles was also observed by transmission electronmicroscopy (TEM, Tecnai G2 20, FEI Company, Hillsboro, Oregon, USA). XPS was used to identify the surface functionalization group concentration (SFGC) of TFPNs. In the reagents for TFPNs preparation, only THFMA contains oxygen element. So the oxygen content on TFPNs surface was used to indirectly represent the SFGC in this work. The XPS measurement was carried out on an ultra-high vacuum(UHV) chamber of the XPS surface analysis system (ESCALAB 250Xi, Thermo Fisher, USA), which was equipped with a monochromatized Al (K $\alpha$ ) X-ray source and operated at 150 W.

## 2.3. Coal flotation using nanoparticles

### 2.3.1. Flotation tests

Flotation experiments were then conducted in a 1.0 dm<sup>3</sup> XFD flotation cell using 70 g of coal. The normal pH of the coal slurry, namely pH=8, was chosen without adding pH regulators. It was consistent with some scholars' works that the coal slurry had the best flotability when pH was neutral or weakly alkaline. 2-octanol was used as the frother with its dosage fixed at 100 g/t. The impeller speed of the flotation machine was set at 1800 rpm and the air flow rate was set at 2 L/min. Slurry was first agitated in the flotation cell for 3 min, after which the polystyrene nanoparticle or diesel oil was added and the slurry was conditioned for an additional period of 5 min. The frother was then added for conditioning for another 1 min. In the end, the flotation was started after introducing air. Froth sample was collected after 3 min of flotation, and the final tailing was collected as well. The collected samples were then filtered, dried and weighed. They were dried at 75°C for 12 hours in a vacuum drying oven. The recovery was calculated using the following equation:

$$\text{recovery (\%)} = M_C / M_F \times 100 \quad (1)$$

where  $M_C$  is weight of the concentrate (%),  $M_F$  is weight of the feed (%).

### 2.3.2. Scanning electron microscope

To gain more information regarding the properties of nanoparticle deposition, images of the recovered concentrates from the flotation tests using nanoparticles were acquired by using an S-3000N (HITACHI, Japan) scanning electron microscope (SEM).

### 2.3.3. Contact angle measurements

Measurements of water contact angle were performed on the coal sample treated by different collectors using DSA100 contact angle analyzer (Kruss, Germany). In each test, 5 g coal (-0.074 mm) was first stirred with a magnetic stirrer in different collector solutions for 30 min. And the suspension was filtered and dried. Then the coal sample was performed at 55 KN for 1 min using a ZHY-601B powder compressing machine (China). The measurements were repeated four times and the average value was used.

### 2.3.4. Fourier transform infrared spectroscopy (FTIR) measurement

Coal sample was conditioned with different collectors for 3 min. After the conditioning processes, the coal sample was filtered and dried at a low temperature of 40°C. Three coal samples were obtained as follows: (A) original coal, (B) coal conditioned with DO, and (C) coal conditioned with TFPNs. For the FTIR analyses, a Perkin Elmer Spectrum 2000 model spectrometer was used and the spectrum was obtained at 2 cm<sup>-1</sup> resolution, between 4000 and 400 cm<sup>-1</sup>. FTIR spectrums of the coal samples were obtained with KBr pellets, prepared with four different coal samples and analytical grade KBr.

## 3. Results and discussion

### 3.1. Nanoparticle properties

The diameter and zeta potential of nanoparticles was shown in Table 2. Particle size and surface characteristics of the nanoparticles play a vital role in adsorption during flotation. The average diameter of the nanoparticles ranges from 50 nm to 138 nm, and it decreases with the CTAB dosage. As the dosage of emulsifier increases, more small micelles will be formed that contribute to the decrease of nanoparticle size. However, the diameters do not show obvious changes with the increase of THFMA dosage. It is indicated that the mean nanoparticle diameter is mainly dominated by CTAB.

Table 2. Recipe for preparation and some properties of nanoparticles

Nanoparticle	Water, g	St, g	DVB, g	CTAB, mg	THFMA, g	V50, g	diameter, nm	zeta potential, mV
St-10-1.48	130	2.73	0.31	10	1.48	0.1	138	26.23
St-30-1.48	130	2.73	0.31	30	1.48	0.1	86	33.11
St-50-1.48	130	2.73	0.31	50	1.48	0.1	77	44.26
St-70-1.48	130	2.73	0.31	70	1.48	0.1	69	48.66
St-100-1.48	130	2.73	0.31	100	1.48	0.1	52	49.62
St-150-1.48	130	2.73	0.31	150	1.48	0.1	50	49.67
St-100-0	130	2.73	0.31	100	0	0.1	53	48.54
St-100-0.37	130	2.73	0.31	100	0.37	0.1	52	48.26
St-100-0.74	130	2.73	0.31	100	0.74	0.1	54	49.23
St-100-2.19	130	2.73	0.31	100	2.19	0.1	53	48.28
St-100-2.92	130	2.73	0.31	100	2.92	0.1	55	49.32

The presence of charged surface groups is critical for maintaining colloidal stable nanoparticles. The zeta potential is a key indicator of the stability of colloidal dispersions. As shown in Table 2, all the nanoparticles display positive zeta potential using CTAB as emulsifier. The positive surface charge of the nanoparticles may be due to the presence of groups of CTAB segments. The zeta potential of

nanoparticles increases with the CTAB dosage, whereas it does not show obvious changes with the increase of THFMA dosage. It is shown that the zeta potential is closely dependent on the concentration of emulsifier selected.

The surface morphology of the nanoparticles was characterized by TEM. It can be seen in Fig. 4 that all the nanoparticles have a nearly-spherical shape and the mean particle size of St-10-1.48 and St-70-1.48 is about 100 nm and 50 nm respectively, which shows agreement with the results obtained from ZetaPALS experiment.

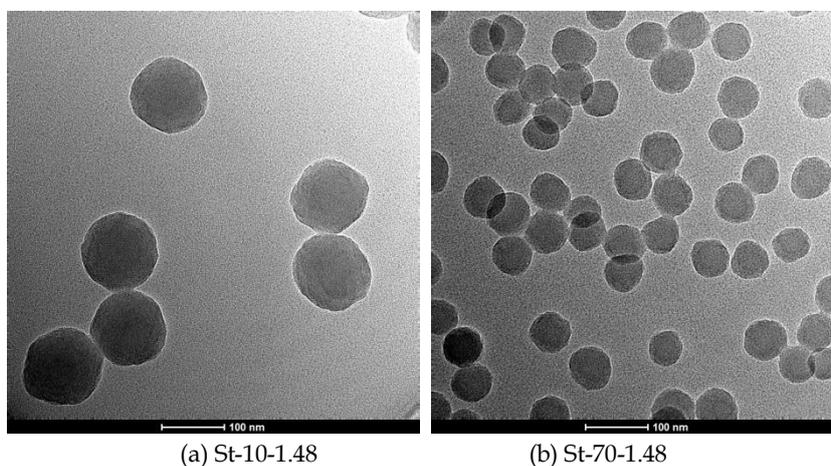


Fig. 4. TEM images of the nanoparticles

The XPS wide energy spectrums of the nanoparticles are shown in Fig. 5. Semi-quantitative results for the surface chemical compositions of nanoparticles, based on the XPS wide energy spectrums, are shown in Table 3. With the dosage of THFMA increasing, the content of element C decreases from 94.22% to 86.90%, while oxygen content increases from 5.78% to 13.10%. These results show that some Tetrahydrofurfuryl functional groups exist on the nanoparticle surface after functionalization and the surface functionalization group concentration (SFGC) increases with the THFMA dosage.

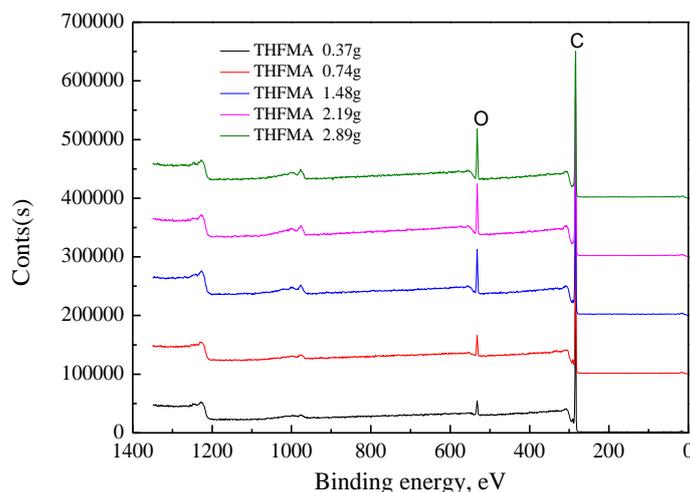


Fig. 5. The XPS C 1s fitting spectra of nanoparticles

Table 3. The relative contents of carbon and oxygen of nanoparticles

THFMA, g	0.37	0.74	1.48	2.19	2.92
C, %	94.22	93.44	88.8	87.96	86.90
O, %	5.78	6.56	11.20	12.04	13.10

### 3.2. Coal flotation performance

Fig. 6 shows the effect nanoparticles size on the low-rank coal flotation recovery. The recovery increases with the decrease of the nanoparticle size. The smallest TFPNs (St-150-1.48, 50 nm) give 68.27% recovery at the dosage of 16 kg/t. By contrast, only 51.23% recovery is obtained using the largest TFPNs (St-10-1.48, 138 nm) at the same dosage. It is possible for smaller TFPNs to decrease the consumption in reaching the same recovery. The obvious conclusion from Fig. 6 is that smaller TFPNs are more effective flotation collectors. This result is consistent with the research of Yang et al (Yang et al., 2012) and Hajati et al (Hajati et al., 2016). They studied the size effects of polystyrene nanoparticles and talc nanoparticles on quartz (glass beads) flotation and also concluded that the quartz recovery increased with decreasing nanoparticle size. It can also be found that the recovery increases with the TFPNs dosage. When small amount of TFPNs is used (8 kg/t), a steep rise in the low-rank coal recovery is observed. By further increasing the TFPNs dosage to 16 kg/t, the recovery tends to increase slightly to reach the maximum recovery. This is probably due to the facts such as nanoparticles aggregation, changing the pulp viscosity, or nanoparticles completely covering coal particle surface.

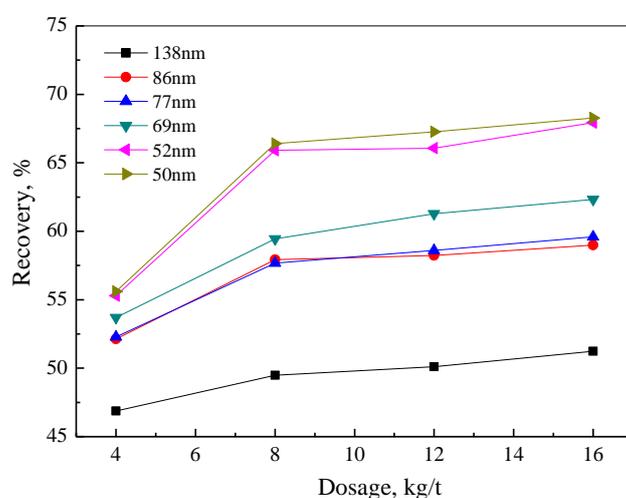


Fig. 6. Effect of nanoparticle size on the low-rank coal flotation performance

The effect of surface functionalization group concentration (SFGC) on the low-rank coal flotation recovery is shown in Fig. 7. As the SFGC increases, the recovery of low-rank coal increases gradually, reaching a maximum of at approximately SFGC 6.56%. Afterwards, the recovery tends to decline steadily at SFGC > 6.56%. It is clear that the optimal SFGC is 6.56%. A good flotation collector must selectively adsorb to low-rank coal particles. In our study, nanoparticle surface was decorated with tetrahydrofurfuryl moieties that interacted specifically with the polar part of low-rank coal surface. The high SFGC means polystyrene nanoparticles surface bearing more tetrahydrofurfuryl groups, which appears to enhance the interaction between the nanoparticle collectors and low-rank coal. However, excessive tetrahydrofurfuryl groups will reduce nanoparticle hydrophobicity producing adverse effect on the attachment of low-rank coal particles to bubbles. Therefore, SFGC has an optimum scope, more or less can not get the ideal result. Similar findings have also been reported for a study by Abarca et al. (Abarca et al., 2015). They found that polymeric nanoparticles require a delicate balance of surface properties to give mineral-specific deposition and colloidal stability, while remaining sufficiently hydrophobic to promote flotation. The results in Fig. 7 also show that the recovery increases with the nanoparticle dosage. This is mainly because more nanoparticles adsorbing on the coal particle surface induces more hydrophobicity to promote the recovery.

Fig. 8 compares the low-rank coal recovery obtained with St-100-0.74, St-100-0 and DO. Both nanoparticles flotation collectors, namely St-100-0.74 and St-100-0, give higher recovery than does the DO, a conventional molecular collector. The recovery of TFPNs (St-100-0.74) is superior to that of PNs (St-100-0). It is indicated that tetrahydrofurfuryl groups can improve the performance of nanoparticles in low-rank coal flotation. The higher recovery with both nanoparticles collectors may be due to a strong

tendency to interact with the coal surface as a result of both hydrophobic bonding and electrostatic attraction with negatively charged coal surface, while there is only hydrophobic bonding between DO and coal surface. Moreover, the interaction between TFPNs with low-rank coal surface exists additional hydrogen bonding from the tetrahydrofurfuryl group compared to the PNs. Therefore electrostatic attraction and hydrogen bonding can promote selective deposition of nanoparticles on low-rank coal.

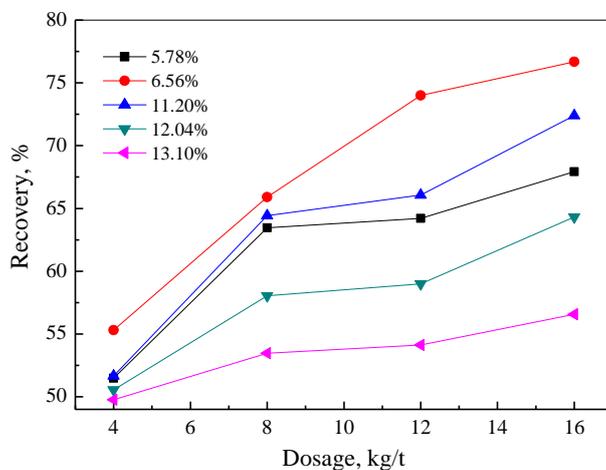


Fig. 7. Effect of nanoparticle SFGC on the low-rank coal flotation performance

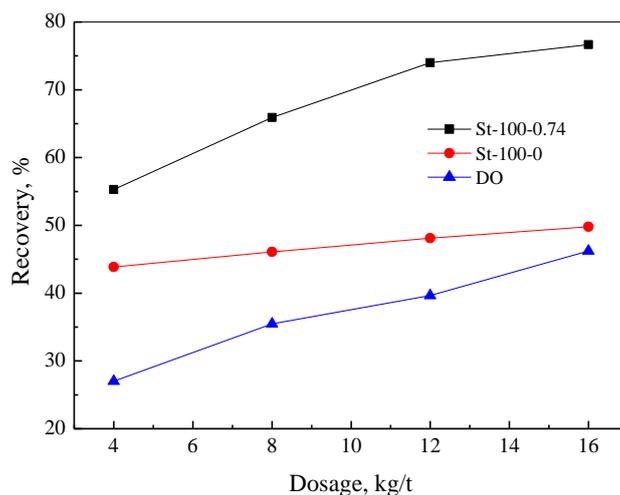


Fig. 8. Comparison of flotation performance between different collectors

### 3.3. Mechanism analysis discussion

Contact angle has been extensively used to characterize the hydrophobicity and floatability of coal samples. To assess the ability of increasing the hydrophobicity of coal surface, the water contact angle of the coal sample treated by different collectors was compared in Fig. 9. The low contact angle of low-rank coal without collector shows that it is extremely hydrophilic. There is a sharp increase in the contact angles of coal sample treated by collectors, indicating the use of the collectors enhances the hydrophobicity of coal surface. As expected, the contact angle of coal sample treated by nanoparticles is larger than that of DO. The contact angle of coal sample treated by nanoparticles increases significantly after decorated with tetrahydrofurfuryl groups. This may be because tetrahydrofurfuryl moieties will promote the nanoparticles to interact specifically with the polar part of low-rank coal surface. However, the contact angle of coal sample treated by St-100-2.92 is smaller than that of St-100-1.48, which may be attributed to the excessive tetrahydrofurfuryl groups that reduce the hydrophobicity of nanoparticles. It can also be found that nanoparticle size can affect the result of contact angle, i.e. the smaller nanoparticles give higher contact angle. This may be due to larger coverage on the coal surface

for smaller nanoparticles at a given dosage. These variations of the contact angle agree well with the above-mentioned flotation results.

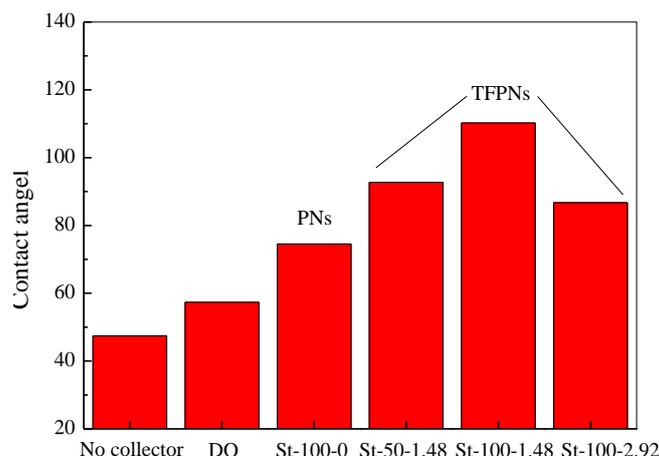


Fig. 9. Contact angle of the coal sample treated by different collectors.

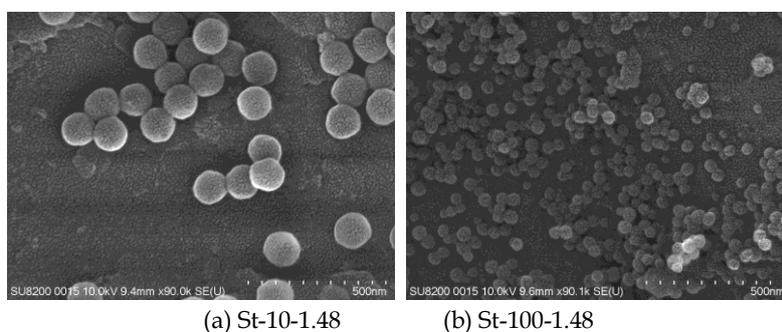


Fig. 10. SEM images of dried concentrate collected after flotation using TFPNs.

Fig. 10 shows the scanning electron microscope (SEM) micrographs of concentrate surface after flotation using the nanoparticles. The easy visualization of nanoparticles on mineral surfaces is one of the advantages of nanoparticle flotation collector that was described in the literature by Yang and Pelton (Yang and Pelton, 2011). As can be seen, the concentrate surface using small nanoparticles has a dense nanoparticle coverage, whereas the nanoparticle density on the concentrate surface using large nanoparticles is sparse. The densely deposited nanoparticles on the coal surface probably contribute to the high contact angle ( $110^\circ$ ) of coal sample treated by nanoparticles as show in Fig. 9. It is proposed that there are some areas of coal between closely spaced nanoparticles that are not wetted when the sessile drop is placed on the dry surface, giving an air/water interface that is typical of superhydrophobic surfaces (Yang and Pelton, 2011). On the other hand, the deposited nanoparticles can increase microscale roughness on the coal surface. A number of studies have suggested that microscale roughness could enhance bubble-particle attachment efficiency. Behzad et al. (Behzad et al., 2016) found that an increase in surface roughness improved the flotation recovery, contact angle, and bubble attachment. Firat and Behzad (Firat and Behzad, 2016) showed that the roughness of particles affected the interaction forces and caused significant improvement in flotation efficiency. In addition, it is worth pointing out the nanoparticles aggregation shown in these micrographs, suggesting that some of the nanoparticles were not colloidally stable under flotation conditions.

To explore the intensification mechanism of low-rank coal flotation by using TFPNs, FTIR experiments were conducted before and after different collectors absorption on low-rank coal surface and the FTIR results are shown in Fig. 11. Peaks at near  $1610\text{cm}^{-1}$ ,  $3430\text{cm}^{-1}$  are corresponding to the vibration of C=O stretching vibration of carboxyl group and O-H stretching vibration of phenolic or alcoholic hydroxyl groups respectively. The -OH, C=O and COOH groups are hydrophilic groups on the coal surface. It is clear that this low-rank coal contains large amounts of oxygen-containing

functional groups -OH, which is correlated with the XPS results. After TFPNs adsorption, the -OH stretching vibration peak and C=O stretching vibration peak is significantly weakened, whereas it does not show obvious changes for DO. This behavior may be attributed to the hydrogen bonding between TFPNs and coal surface, as shown in Fig. 12. The reduction of the hydrophilic group can increase the surface hydrophobicity and floatability of coal particle. The peaks changes for these hydrophilic groups with the TFPNs is greater than that with DO, which illustrated that TFPNs could make the low-rank coal more hydrophobic than conventional DO.

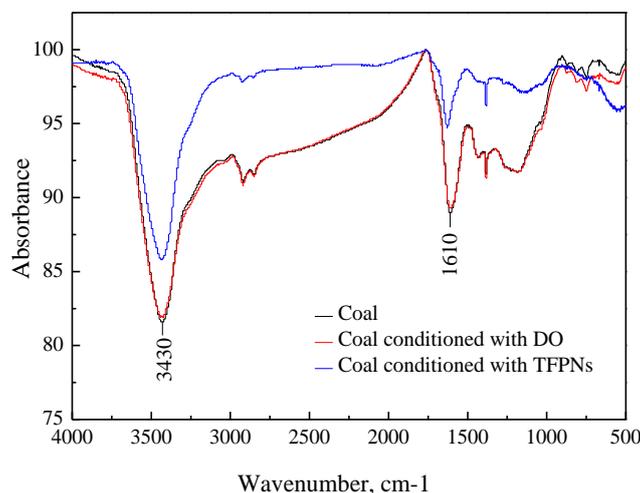


Fig. 11. FTIR results of coal before and after different collectors adsorption.

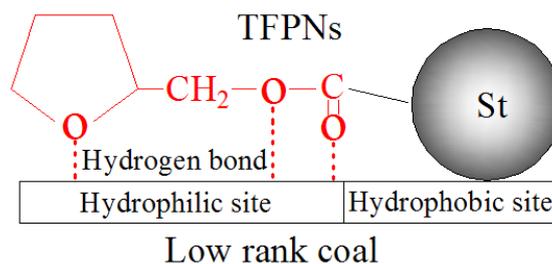


Fig. 12. Interaction mechanism of the TFPNs on the low rank coal surface.

There are three key requirements for nanoparticle flotation collectors (Abarca et al., 2015; Abarca et al., 2018; Abarca et al., 2017): (1) the nanoparticles must be colloidally stable in the flotation medium; (2) the nanoparticles must be sufficiently hydrophobic so that mineral particles decorated with adsorbed nanoparticles will attach to air bubbles; and, (3) the nanoparticles must bear surface functionalities that promote selective deposition onto the desired minerals surfaces. To confer colloidal stability and promote nanoparticle deposition onto low-rank coal, nanoparticle surfaces are decorated with up to tetrahydrofurfuryl groups that interact specifically with oxygen-containing functional groups. But the surface functionalization group concentration (SFGC) has an optimum scope. Less surface functionalization group is detrimental to mineral-specific deposition and colloidal stability, whereas more surface functionalization group decrease hydrophobicity. Nanoparticles flotation collectors require a delicate balance of surface properties to give mineral-specific deposition and colloidal stability in the flotation media, while remaining sufficiently hydrophobic to promote flotation. In this study, the effect of polystyrene nanoparticle parameters such as SFGC, particle size and dosage on the low-rank coal flotation performance was investigated and optimized. Through the research, TFPNs can specifically deposit onto the low-rank coal particles with the hydrogen bonding function between tetrahydrofurfuryl groups and oxygen-containing functional groups, and enhance low-rank coal flotation by increasing the hydrophobicity and roughness of coal particle with the adsorbed nanoparticles, even if there is some nanoparticles aggregation under flotation conditions. Therefore, TFPNs are introduced as a new class of collectors for low rank coal flotation.

#### 4. Conclusions

TFPNs were prepared and used as collectors in low-rank coal flotation. The effect of several parameters such as SFGC, particle size and dosage on flotation performance was investigated. The interaction mechanism between TFPNs and low-rank coal was also discussed. The main conclusions from this work are the following:

(1) TFPNs had a nearly-spherical shape and display positive zeta potential, with the mean diameter of 50-138 nm. Both the particle size and zeta potential were closely dependent on the CTAB concentration. The SFGC increased with the THFMA dosage.

(2) TFPNs gave higher recovery than that given by PNs and DO. Smaller nanoparticles were more effective flotation collectors. The recovery increased firstly and then decreased with SFGC. SFGC had an optimum scope, more or less could not get the ideal result. The variations of contact angle of the coal sample treated by different collectors agreed well with the flotation results.

(3) Although there was some aggregation under flotation conditions, TFPNs can specifically deposit onto the low-rank coal particles with the hydrogen bonding function between tetrahydrofurfuryl groups and oxygen-containing functional groups, and promote low-rank coal flotation by increasing the hydrophobicity and roughness of coal particle with the adsorbed nanoparticles, which introduced a new class of collectors for low rank coal flotation.

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