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The Effect of Conditioning on the Flotation of Pyrrhotite in the Presence of Chlorite

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Abstract: The influence of conditioning on the flotation of pyrrhotite in the presence of chlorite was investigated through flotation tests, sedimentation tests, and X-ray photoelectron spectroscopy (XPS) analysis. The flotation results show that chlorite slimes dramatically impair the flotation of pyrrhotite. Sedimentation and flotation tests reveal that conditioning can effectively remove chlorite slimes from pyrrhotite surfaces, resulting in an enhanced flotation recovery of pyrrhotite. When mixed minerals were conditioned under the natural atmosphere, a faster conditioning speed and longer conditioning time decreased the flotation recovery of pyrrhotite. However, when mixed minerals were conditioned under a nitrogen atmosphere, a more intensive conditioning process provided better flotation results. XPS analyses illustrate that a faster conditioning speed and longer conditioning time under the natural atmosphere accelerates the oxidation of pyrrhotite, leading to a decrease in the flotation recovery of pyrrhotite.

Keywords: conditioning; pyrrhotite; chlorite; flotation

1. Introduction

Chlorite, as a typical magnesium-rich phyllosilicate mineral, widely exists in many metal sulfide ore deposits [1]. In sulfide flotation, magnesium silicate (MgO) gangue minerals containing chlorite are known to cause problems by adhering to valuable mineral particles in “hetero-aggregation or slime coating” due to the differences in surface charges [2,3]. Coating of chlorite slime particles on sulfide mineral surfaces will decrease the hydrophobicity of the sulfide mineral and may also reduce the collector adsorption, which will result in lower recoveries of the valuable sulfide minerals [4,5].

Pyrrhotite is one of the most abundant sulfide minerals [6]. Furthermore, it is often found in nickel sulfide ores and associated with valuable minerals, which suggests that pyrrhotite losses result in significant losses of nickel minerals [7].

In order to improve the flotation recoveries of the sulfide mineral, the effect of both conditioning speed and conditioning time was observed in the flotation process [8–10]. Zhang et al. achieved better carbon flotation recovery and separation efficiency by increasing the intensity of conditioning [11]. Bulatovic found that conditioning could improve the flotation recovery of copper-nickel sulfide ores and copper-zinc sulfide ores in addition to concentrating the grade [12,13]. Feng et al. studied the effect of high intensity conditioning on the flotation of sulfide and found that high intensity conditioning could significantly increase the flotation recovery of copper-nickel sulfide ores [14]. However, the influence of conditioning on the flotation of pyrrhotite in the presence of chlorite has not been investigated.

In this paper, the influence of conditioning on the flotation of pyrrhotite in the presence of chlorite was studied. Furthermore, the interacting mechanisms were also discussed for providing guidance for further study.
2. Materials and Methods

2.1. Samples and Reagents

A chunk of the sample containing unliberated pyrrhotite minerals was obtained from the Tongling mine located in Anhui, China. The collected sample was hammered into small pieces to liberate the pyrrhotite minerals, which were sorted out based on the color differences. X-ray diffraction analyses (Figure 1) of the hand-sorted pyrrhotite concentrates indicated that the sample was of considerably high purity with trace amounts of pyrite. The dry sample was ground in a lab-scale ball mill using ceramic media to eliminate contaminations. The ground sample was screened into different size fractions using sieves with 150 \( \mu \text{m} \) and 38 \( \mu \text{m} \) opening sizes. The \(-150 + 38 \mu \text{m}\) size fraction was utilized for the current study.

A chunk of the sample containing unliberated chlorite minerals was also obtained from the Haicheng mine located in Liaoning, China. The collected sample was hammered into small pieces to liberate the chlorite minerals, which were sorted based on the color differences. X-ray diffraction analyses (Figure 2) and elemental analyses (Table 1) of the hand-sorted chlorite concentrate indicated that the sample was of considerably high purity with trace amounts of talc. The dry sample was ground in a lab-scale ball mill using ceramic media to eliminate contaminations. The ground sample was screened into different size fractions using a sieve with 38 \( \mu \text{m} \) opening size. The \(-38 \mu \text{m}\) size fraction was utilized for the current study.

MIBC (methyl isobutyl carbinol) purchased from Tianjin Guangfu Fine Chemical Research Institute, Tianjin, China was used as the frother. KOH (potassium hydroxide) was used as pH regulators. All the reagents used in the current study were of analytical grade except for the potassium amyl xanthate (PAX), which was of chemical grade and used as the collector. Deionized double distilled water was used for all tests.

![Figure 1. X-ray diffraction (XRD) pattern of the pyrrhotite sample.](image)

<table>
<thead>
<tr>
<th>Composition</th>
<th>MgO</th>
<th>SiO(_2)</th>
<th>Al(_2)O(_3)</th>
<th>CaO</th>
<th>TFe</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Percentage/%</td>
<td>25.41</td>
<td>34.37</td>
<td>15.76</td>
<td>0.78</td>
<td>3.72</td>
<td>19.96</td>
</tr>
</tbody>
</table>

Table 1. Chemical compositions of chlorite.
2.2. Experiments

2.2.1. Flotation Tests

Flotation tests were conducted in a XFG type mechanical agitation flotation machine equipped with a flotation cell of 40 mL. For each test, 2.0 g of minerals was mixed and dispersed in 40 mL of distilled water in the flotation cell. The slurry was adjusted to a desired value of 9 by adding KOH solution at a concentration of \(1 \times 10^{-5}\) mol/L, before this mixture was conditioned for a desired period of time and at a given speed. To test the effects of chlorite on the flotation performance of pyrrhotite, chlorite was added at the beginning of the conditioning process. Control tests were conducted by introducing nitrogen into the pulp throughout the conditioning process to examine the effects of natural atmosphere on pyrrhotite flotation. The prepared PAX (Potassium Amyl Xanthate) solution was added at a desired concentration of \(1 \times 10^{-4}\) mol/L and conditioned for 3 min. After that, the agitation speed was adjusted to 1500 rpm, MIBC was added to the slurry at a desired concentration of \(1 \times 10^{-4}\) mol/L and conditioned for 1 min. Following this, flotation was performed at this agitation speed. Each flotation test was performed for 5 min and five concentrates were collected after cumulative times of 1, 2, 3, 4, and 5 min. The dry weights of the concentrate and tail were measured and used to calculate the recovery. Each flotation test was measured three times and the average was reported as the final value. The standard deviation, which is presented as an error bar, was obtained using the mean of the three measurements per experimental condition.

2.2.2. Sedimentation Tests

Flocculation/dispersion behaviors of the mixed minerals (pyrrhotite/chlorite = 10:1) in solution were investigated through settling tests, which were conducted in a graduated cylinder. A total of 1 g of mixed minerals were conditioned in the flotation cell at a desired conditioning speed for 5 min at a pH of 9. Afterwards, the suspension was transferred to a 100-mL cylinder and distilled water was added to bring the water level to 100 mL. The cylinder was stoppered, inverted 20 times, and then set still in an upright position for 3 min. Suspension of the upper 25 mL of the solution was siphoned out and turbidity of the sample was measured utilizing a WGZ-3(3A) type Scattering Turbidimeter, which is made by the Shanghai Xinrui Instrument Company (Shanghai, China). The degree of flocculation/dispersion was characterized by the turbidity of the supernatant liquor. A lower turbidity value normally indicates a higher degree of flocculation associated with particles in slurries.

2.2.3. XPS Analysis

To detect the change in chemical information of the species located on the surface, the pyrrhotite samples were treated at the desired conditioning speed and for the desired period of time. If necessary, nitrogen was introduced into the pulp to protect pyrrhotite from oxidation during conditioning process.
pyrrhotite and mixed minerals were performed. Both samples were conditioned at a pH of 9 and a
conditioning was employed. In the process of conditioning, the mineral particles yield fluid force in
the flowing pulp. Under these conditions, the sulfide particles and the slime particles have different
kinematic velocities due to their different weights and fluid forces. Thus, when the differences in fluid
forces imposed on the sulfide and the slime particles exceed the attraction forces between them, the
slime particles fall off from the sulfide particles and flowed with the pulp. Therefore, the detachment
of chlorite from pyrrhotite surfaces can be realized through conditioning [9,10]. The removal of fine
as a contrast. To prevent surface oxidization, the samples were stored in a vacuum drier. The XPS
measurements were performed using PHI5000 Versa Probe II (PHI5000, ULVAC-PHI, Chigasaki,
Japan). The samples were subjected to a survey scan to first identify chemical components, before
high-resolution scans were conducted, focusing on certain elements. The spectra and surface atomic
ratios were obtained and calculated based on the XPS PEAK software programmed by Raymond
Kwok. Sample charging was compensated by taking the C 1s peak of background hydrocarbon at
284.8 eV as an internal standard.

3. Results and Discussion
Since chlorite is of low hardness, the production of slimes may interfere with the flotation of
pyrrhotite. Figure 3 shows the flotation recovery of pyrrhotite and grade of sulfur as a function of the
amount of chlorite at a pH of 9. As shown in Figure 3, the flotation recovery of pyrrhotite in the absence
of chlorite is very high (about 85%). Upon the addition of chlorite particles, the recovery of pyrrhotite
decreases dramatically with an increase in the amount of chlorite particles. When the amount of
chlorite reaches 10% or above, the flotation of pyrrhotite was depressed drastically. Nevertheless, the
addition of chlorite makes no difference to the sulfur grade.

![Figure 3. Effect of chlorite on the flotation recovery of pyrrhotite and grade of sulfide (pH = 9.0 ± 0.2;
C(potassium amylxanthate) = 1 \times 10^{-4} \text{ mol/L}; C(methyl isobutyl carbinol (MIBC))= 1 \times 10^{-4} \text{ mol/L}).](image)

To study the effect of chlorite on the depression on pyrrhotite, the XPS measurements of single
pyrrhotite and mixed minerals were performed. Both samples were conditioned at a pH of 9 and a
speed of 1500 rpm for 5 min, before being dried in a vacuum drier. For the mixed minerals, we used a
magnet to concentrate pyrrhotite, before the solution was rinsed three times with distilled water to
remove chlorite by entrainment. Broad-scan XPS results for pyrrhotite and mixed minerals are shown
in Figure 4. The two spectra are similar with one major difference. The characteristic peaks for Mg
and Si are only observed in the spectra b in Figure 4, which shows that chlorite slimes adhere to the
surface of pyrrhotite and restricts the adsorption of xanthate onto the surface of pyrrhotite. Hence, the
flotation recovery of pyrrhotite decreases [15].

Conditioning refers to the initial suspension and agitation stage (in preparation for the flotation
process) for the finely-ground minerals in water with reagents. It is known that conditioning could
desorb slimes from valuable minerals [14]. Thus, to eliminate the adverse effect of chlorite slimes,
conditioning was employed. In the process of conditioning, the mineral particles yield fluid force in
the flowing pulp. Under these conditions, the sulfide particles and the slime particles have different
kinematic velocities due to their different weights and fluid forces. Thus, when the differences in fluid
forces imposed on the sulfide and the slime particles exceed the attraction forces between them, the
slime particles fall off from the sulfide particles and flowed with the pulp. Therefore, the detachment
of chlorite from pyrrhotite surfaces can be realized through conditioning [9,10]. The removal of fine
chlorite particles from pyrrhotite surfaces increases the adsorption density of xanthate and improves its flotation performance [16,17].

Figure 4. Broad scan X-ray photoelectron spectroscopy (XPS) spectra for: (a) pyrrhotite and (b) mixed minerals (pyrrhotite/chlorite = 10:1) at a pH of 9 and a speed of 1500 rpm for 5 min.

Figure 5 shows the effect of conditioning speed and time on the turbidity of pyrrhotite and chlorite slurries. Higher turbidity values indicate a more efficient removal of chlorite slimes from pyrrhotite surfaces. As seen from Figure 5, conditioning can effectively remove chlorite slimes from pyrrhotite surfaces. A faster conditioning speed and longer conditioning time led to higher turbidity values and thus, more efficient chlorite detachment. In order to detect the influence of conditioning on the flotation recovery of pyrrhotite in the presence of chlorite, flotation tests were performed.

Figure 5. Turbidity of mixed minerals (pyrrhotite and chlorite were mixed by 10:1) as a function of conditioning speed and time of pH = 9.0 ± 0.2.

Figure 6 demonstrates the effect of conditioning speed on the pyrrhotite recovery under the conditioning time of 5 min. The results illustrate that conditioning can dramatically improve the flotation recovery and the best result was obtained with a conditioning speed of 2000 rpm. When the conditioning speed was increased up to 2500 rpm, the flotation recovery of pyrrhotite decreased.

In addition, in regard to the flotation tests examining the effect of conditioning time on the pyrrhotite recovery under the conditioning speed of 2000 rpm, the similar results obtained show that
the best flotation performance was achieved under the conditioning time of 5 min. Overall, a longer conditioning time decreased flotation recovery (Figure 7).

Previous studies indicated that conditioning increases sulfide mineral flotation recovery significantly, with better flotation performance able to be realized using a longer conditioning time and strong conditioning intensity [8,14]. This is not completely consistent with the results shown in Figures 6 and 7.

Pyrrhotite can rapidly react with water and dissolved oxygen in pulp [18]. The rapid oxidation of pyrrhotite will lead to the formation of hydrophilic iron hydroxides, which will coat pyrrhotite surfaces. As such, the adsorption density of xanthate on pyrrhotite surfaces will decrease and the pyrrhotite floatability will be impaired [7,19–22]. This may be the reason why a faster conditioning speed and longer conditioning time decreased flotation recovery (Figure 7).

![Figure 6](image1.png)

**Figure 6.** Effect of conditioning speed under natural atmosphere on the recovery of mixed minerals, with pyrrhotite and chlorite mixed at a ratio of 10:1 (pH = 9.0 ± 0.2; C(potassium amyl xanthate) = 1 × 10^{-4} mol/L; C(MIBC) = 1 × 10^{-4} mol/L; and Conditioning time = 5 min).

![Figure 7](image2.png)

**Figure 7.** Effect of conditioning time under natural atmosphere on the recovery of mixed minerals, with pyrrhotite and chlorite mixed at a ratio of 10:1 (pH = 9.0 ± 0.2; C(potassium amyl xanthate) = 1 × 10^{-4} mol/L; C(MIBC) = 1 × 10^{-4} mol/L; and Conditioning time = 5 min).
conditioning process, which is congruent with the sedimentation test results. Furthermore, at the same conditioning speed and for the same period of time, the flotation recovery of pyrrhotite conditioned under the nitrogen atmosphere is higher than that under natural atmosphere. Thus, this reveals that oxygen may interfere with pyrrhotite flotation performance, leading to a decrease in pyrrhotite flotation recovery.

![Diagram](image)

**Figure 8.** Effect of conditioning speed under nitrogen atmosphere on the recovery of mixed minerals, with pyrrhotite and chlorite mixed at a ratio of 10:1 (pH = 9.0 ± 0.2; C(potassium amyl xanthate) = 1 × 10^{-4} \text{ mol/L}; C(MIBC) = 1 × 10^{-4} \text{ mol/L}; and Conditioning time = 5 min).

![Diagram](image)

**Figure 9.** Effect of conditioning time under nitrogen atmosphere on the recovery of mixed minerals, with pyrrhotite and chlorite mixed at a ratio of 10:1 (pH = 9.0 ± 0.2; C(potassium amyl xanthate) = 1 × 10^{-4} \text{ mol/L}; C(MIBC) = 1 × 10^{-4} \text{ mol/L}; and Conditioning time = 5 min).

In order to detect the chemical information of the species on the surface, the pyrrhotite samples treated under different conditions were examined by X-ray photoelectron spectroscopy (XPS). The Fe and S oxidation states on pyrrhotite surfaces were analyzed. The obtained spectra were fitted and the relative contents of different compositions were determined by the XPSPEAK software.

As shown in Figure 10, the Fe2p spectra of pyrrhotite samples treated without conditioning, treated with conditioning under the natural atmosphere for 20 min, and treated with conditioning under nitrogen atmosphere for 20 min are composed of five peaks at (A) 712.30 eV, (B) 711.50 eV, (C) 710.60 eV, (D) 710.00 eV, and (E) 713.00 eV, respectively. By comparing the binding energy values
of Fe2p with those from references, the peaks A, B, C, D, and E are attributed to Fe$_2$(S$_x$)$_3$, FeOOH, Fe$_2$O$_3$, FeS, and Fe$_2$(SO$_4$)$_3$, respectively [23–25]. As can be seen from Figure 10 and Table 2, the Fe species of the untreated pyrrhotite surfaces mainly consist of Fe$_2$(S$_x$)$_3$, FeOOH, Fe$_2$O$_3$, and FeS, the relative contents of which are 45.83%, 21.95%, 15.78%, and 16.44%, respectively. For the surfaces of the pyrrhotite treated with conditioning under the natural atmosphere for 20 min, the new species of Fe$_2$(SO$_4$)$_3$ formed with a relative content of 25.28%. Moreover, by comparison with the untreated pyrrhotite, the relative contents of FeOOH and Fe$_2$O$_3$ on pyrrhotite surfaces that are treated with conditioning under the natural atmosphere increase up to 31.20% and 24.43%, respectively. This may indicate that the content of Fe$^{3+}$ on the surface of pyrrhotite increases, perhaps due to the oxidation of Fe$^{2+}$ when in contact with oxygen [26]. However, when the pyrrhotite is treated with conditioning under the nitrogen atmosphere for 20 min, the Fe species and their relative contents are similar to that of untreated pyrrhotite.

![Figure 10. Fe2p spectra for the pyrrhotite surface treated: (a) without conditioning; (b) with conditioning under the natural atmosphere for 20 min; and (c) with conditioning under the nitrogen atmosphere for 20 min.](image-url)
According to Figure 11, the S2p spectra of pyrrhotite samples not treated with conditioning, treated with conditioning under the natural atmosphere for 20 min, and treated with conditioning under the nitrogen atmosphere for 20 min are composed of four peaks at (A) 161.30 eV, (B) 162.60 eV, (C) 163.80 eV, and (D) 168.50 eV, respectively. By comparing the binding energy values of S2p with those from references, the peaks A, B, C, and D are attributed to FeS, Fe$_2$(S$_x$)$_3$, S$^0$, and Fe$_2$(SO$_4$)$_3$, respectively [24,25,27]. As seen from Figure 11 and Table 3, the S species of the untreated pyrrhotite surfaces mainly consist of FeS, Fe$_2$(S$_x$)$_3$, and S$^0$, with the relative contents of these being about 33%. For the surfaces of the pyrrhotite treated with conditioning under the natural atmosphere for 20 min, the new species Fe$_2$(SO$_4$)$_3$ occurs at a relevant content of 15.38%, which is likely due to the oxidation of the pyrrhotite. However, when the pyrrhotite is conditioned under the nitrogen atmosphere for 20 min, the Fe species and their relevant contents are similar to that of untreated pyrrhotite.

**Table 2.** Fe species binding energy (eV) and relative contents (%) for the pyrrhotite surface treated with different types of conditioning.

<table>
<thead>
<tr>
<th>Peak</th>
<th>Fe Species</th>
<th>Without Conditioning</th>
<th>Conditioning under Natural Atmosphere for 20 min</th>
<th>Conditioning under Nitrogen Atmosphere for 20 min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Binding Energy (eV)</td>
<td>Relative Contents (%)</td>
<td>Binding Energy (eV)</td>
<td>Relative Contents (%)</td>
</tr>
<tr>
<td>A</td>
<td>Fe$_2$(S$_x$)$_3$</td>
<td>712.40</td>
<td>45.83</td>
<td>712.30</td>
</tr>
<tr>
<td>B</td>
<td>FeOOH</td>
<td>711.45</td>
<td>21.95</td>
<td>711.41</td>
</tr>
<tr>
<td>C</td>
<td>Fe$_2$O$_3$</td>
<td>710.72</td>
<td>15.78</td>
<td>710.42</td>
</tr>
<tr>
<td>D</td>
<td>FeS</td>
<td>710.07</td>
<td>16.44</td>
<td>–</td>
</tr>
<tr>
<td>E</td>
<td>Fe$_2$(SO$_4$)$_3$</td>
<td>–</td>
<td>–</td>
<td>713.15</td>
</tr>
</tbody>
</table>

**Figure 11.** Cont.
results of this investigation, the following conclusions can be drawn: The current study systematically investigated the influence of conditioning on the pyrrhotite flotation performance in the presence of chlorite under different air conditions, which explained the interaction mechanisms of conditioning and provided a reference for further study. Based on the results of this investigation, the following conclusions can be drawn:

1. In pyrrhotite flotation, chlorite slimes impairs pyrrhotite flotation performance due to the surface coating.

Pyrrophite is a reactive sulfide mineral and is highly prone to oxidation [6,22]. The extent of oxidation affects the flotation performance of pyrrhotite. Oxidation of the pyrrhotite may occur during all stages in the process involving conditioning [28]. The general oxidation mechanisms can be described as

\[
\text{Fe}_{1-x}S + (2 - (1/2)x)O_2 + xH_2O \rightarrow (1 - x)\text{Fe}^{2+} + x\text{SO}_4^{2-} + 2xH^+ \quad (1)
\]

\[
\text{Fe}^{2+} + 1/4O_2 + H^+ \rightarrow \text{Fe}^{3+} + 1/2H_2O \quad (2)
\]

It is generally believed that the main oxidant agent in pyrrhotite slurry is the dissolved oxygen from atmosphere. Thus, the concentration of dissolved oxygen will influence the rate of pyrrhotite oxidation [18,20,21,29]. A faster conditioning speed and longer conditioning time increase the amount of dissolved oxygen in the pulp and thus accelerate pyrrhotite oxidation. Therefore, the hydrophilic iron hydroxides formed through pyrrhotite oxidization coat the surface of pyrrhotite, reducing the adsorption of xanthate onto pyrrhotite surfaces. As a result, the flotation recovery of pyrrhotite is decreased.

4. Conclusions

The current study systematically investigated the influence of conditioning on the pyrrhotite flotation performance in the presence of chlorite under different air conditions, which explained the interaction mechanisms of conditioning and provided a reference for further study. Based on the results of this investigation, the following conclusions can be drawn:

1. In pyrrhotite flotation, chlorite slimes impair pyrrhotite flotation performance due to the surface coating.

Figure 11. S2p spectra for the pyrrhotite surface treated: (a) without conditioning; (b) with conditioning under the natural atmosphere for 20 min; and (c) with conditioning under the nitrogen atmosphere for 20 min.

Table 3. S species binding energy (eV) and relative contents (%) for the pyrrhotite surface treated with different types of conditioning.

<table>
<thead>
<tr>
<th>Peak</th>
<th>S Species</th>
<th>Without Conditioning</th>
<th>Conditioning under Natural Atmosphere for 20min</th>
<th>Conditioning under Nitrogen Atmosphere for 20min</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Binding Energy (eV)</td>
<td>Relative Contents (%)</td>
<td>Binding Energy (eV)</td>
</tr>
<tr>
<td>A</td>
<td>FeS</td>
<td>161.29</td>
<td>33.80</td>
<td>161.24</td>
</tr>
<tr>
<td>B</td>
<td>Fe$_2$(S$_x$)$_3$</td>
<td>166.42</td>
<td>33.44</td>
<td>166.41</td>
</tr>
<tr>
<td>C</td>
<td>S$_0$</td>
<td>163.65</td>
<td>32.76</td>
<td>163.96</td>
</tr>
<tr>
<td>D</td>
<td>Fe$_2$(SO$_4$)$_3$</td>
<td>–</td>
<td>–</td>
<td>168.36</td>
</tr>
</tbody>
</table>

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2. Conditioning can effectively detach chlorite slimes from pyrrhotite surfaces, resulting in enhanced flotation recovery of pyrrhotite. When mixed minerals were conditioned under the natural atmosphere, a faster conditioning speed and longer conditioning time decreased pyrrhotite flotation recovery to some degree. However, when mixed minerals were conditioned under a nitrogen atmosphere, a faster conditioning speed and longer conditioning time gave better flotation results.

3. XPS analysis shows that when mixed minerals were conditioned under the natural atmosphere, a faster conditioning speed and longer conditioning time accelerates the pyrrhotite surface oxidization, which results in a decrease in pyrrhotite flotation recovery.

4. The industrial tests of nickel sulfide ores under nitrogen atmosphere have not been performed, which will be the focus of the following study.

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Author Contributions: Qing Shi conceived and designed the experiments; Yanfei Chen performed the experiments; Qing Shi and Yanfei Chen analyzed the data; Qingming Feng, Yiping Lu and Qing Shi contributed reagents/materials/analysis tools; Yanfei Chen, Qing Shi, Qiming Feng, Yiping Lu and Wencai Zhang wrote and revised the paper.

Conflicts of Interest: The authors declare no conflict of interest.

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