Effect of Nanobubbles on the Flotation Performance of Oxidized Coal

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1. INTRODUCTION

As a globally important fossil energy and chemical raw material, coal occupies an important position in the energy industry in many countries, especially in China.1 However, the coal could be oxidized during the processes of storage, transportation, and handling, leading to the poor combustibility because it may contain a developed pore structure and abundant oxygen-containing functional groups, which result in a low attachment efficiency.6

In the flotation process, the hydrophobic coal particles could be attached to air bubbles and be transported into the froth layer, while the hydrophilic gangue will be remained in the slurry. The oxidized coal has poor floatability because it contains a developed pore structure and abundant oxygen-containing functional groups, which result in a low attachment probability to the air bubbles and thus low flotation efficiency.6 Therefore, it is important to develop a flotation process to enhance the attachment efficiency between oxidized coal particles and bubbles.

To this end, many studies have focused on the methods to enhance the flotation performance of oxidized coal, such as grinding,7 thermal pretreatment,8 and microwave9 and ultrasonic particle surface pretreatment.10 These methods could improve the floatability by removing surface oxygen groups. However, surface pretreatment can eliminate limitedly the oxygenated functional groups on the coal surface.11 Recently, scholars have focused on the effect of reducing the bubble size on fine mineral flotation, and nanobubbles have been used in mineral flotation.

Nanobubbles are gas cavities with a radius of approximately tens to hundreds of nanometers. Surface nanobubbles were first speculated to exist by Parker et al.12 based on stepwise features in force curves between two hydrophobic surfaces. Surface nanobubbles can survive from hours to days.13 Nanobubbles have longevity seems to be paradoxical, as a simple classical (Epstein–Plesset theory) estimate suggests that they should dissolve in microseconds due to the large Laplace pressure inside these nanoscopic spherical-cap-shaped objects. Many theories have been put forward to explain the unusual stability of nanobubbles, among which the most successful ones include the contamination model,14 dynamic saturation model, and contact line pinning and supersaturation model. However, many scholars found that the contaminant layer model may not explain the stability of the nanobubbles.15 Brenner and Lohse16 proposed a dynamic equilibrium model to explain the stability of nanobubbles, gas

ABSTRACT: In this study, the effects of air bubbles and nanobubbles on flotation performance and kinetics of oxidized coal were investigated. The surface properties of the coal sample before and after oxidation were characterized by a scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). The nanobubbles on highly oriented pyrolytic graphite (HOPG) were observed by an atomic force microscope (AFM). The interaction between coal and conventional bubbles in the absence and presence of nanobubbles was explained by induction time. Flotation results showed that oxidized coal flotation in the presence of nanobubbles resulted in 10% higher combustible matter recovery than conventional air bubble flotation. Moreover, it was found that the flotation of oxidized coal in the absence and presence of nanobubbles can be best described using the first-order model with the rectangular model. AFM images analysis showed that a large number of nanobubbles were produced and attached to the oxidized coal surface. The induction times of the oxidized coal in the absence and presence of nanobubbles were 1000 and 39 ms, respectively, indicating that the existence of nanobubbles effectively promotes the interaction between oxidized coal and macroair bubbles. In addition, the agglomeration between oxidized coal particles also occurred spontaneously in the presence of nanobubbles, which was helpful in improving the combustible matter recovery and flotation rate of oxidized coal.
could pass through the gas–liquid boundary and maintain dynamic equilibrium. However, the fatal flaw of the dynamic equilibrium theory is that its driving mechanism is not clear. The contact line pinning and supersaturation model is the most reasonable theory to explain the stability of nanobubbles. Many researchers have studied this theory. Pinning implies that if the nanobubble expansion result in height increases, which resulting in the Laplace pressure of the nanobubble less than the surface tension of the bubble, thus the height of the bubble will decrease. On the contrary, if the nanobubble height decreases, the Laplace pressure of the bubble will be greater than the surface tension of the nanobubble, counteracting a further decrease. Therefore, pinning provides a negative feedback that is in the process of nanobubble expansion or contraction to keep the nanobubble stable. There are many ways to produce nanobubbles and microbubbles such as temperature difference, differential pressure, and changing the chemical composition of the solution to reduce the solubility of air. In our study, we produce nanobubbles by the temperature difference method. The advantage of the temperature difference method is that no organic solvents are used in this procedure, which avoids some potential risk of contaminations from the organic solvent. Zhang et al. proved that the temperature difference method can generate nanobubbles, and they applied a degassing method to prove what formed on the graphite surface were gaseous bubbles or layers, which may indicate what the authors observed by AFM would likely to be nanobubbles, not contamination. Then, they found that the magnitude of the adhesion has also increased between carbon sphere and surface of HOPG after the formation of nanobubbles. The main advantages of nanobubbles are their higher surface tension than the surface tension of the nanobubble, counteracting a further decrease. On the contrary, if the nanobubble height increases, the surface tension of the bubble is less than the surface tension of the nanobubble, thus the height of the nanobubble will be greater. Many researchers have studied this theory. Pinning implies that if the nanobubble expansion result in height increases, which resulting in the Laplace pressure of the nanobubble less than the surface tension of the bubble, thus the height of the bubble will decrease. On the contrary, if the nanobubble height decreases, the Laplace pressure of the bubble will be greater than the surface tension of the nanobubble, counteracting a further decrease. Therefore, pinning provides a negative feedback that is in the process of nanobubble expansion or contraction to keep the nanobubble stable. There are many ways to produce nanobubbles and microbubbles such as temperature difference, differential pressure, and changing the chemical composition of the solution to reduce the solubility of air. In our study, we produce nanobubbles by the temperature difference method. The advantage of the temperature difference method is that no organic solvents are used in this procedure, which avoids some potential risk of contaminations from the organic solvent. Zhang et al. proved that the temperature difference method can generate nanobubbles, and they applied a degassing method to prove what formed on the graphite surface were gaseous bubbles or layers, which may indicate what the authors observed by AFM would likely to be nanobubbles, not contamination. Then, they found that the magnitude of the adhesion has also increased between carbon sphere and surface of HOPG after the formation of nanobubbles. The main advantages of nanobubbles are their higher surface tension than the surface tension of the nanobubble, counteracting a further decrease. On the contrary, if the nanobubble height increases, the surface tension of the bubble is less than the surface tension of the nanobubble, thus the height of the nanobubble will be greater.

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Here, $\Delta T_{\text{cold}} = 20 - 7^\circ C$, $\Delta T_{\text{hot}} = (T_{\text{hot}} - 20)^\circ C$, and $V_{\text{cold}}/V_{\text{hot}} = \gamma_{\text{f}}$, as the temperature of hot water, $T_{\text{hot}} = 59^\circ C$, and the volumes of the cold water and hot water were in the ratio 3:1.

After each experiment, the concentrates and tailings were filtered and dried in an oven at 80 °C, and the ash content was measured using a muffle furnace. Finally, the floatation combustible matter recovery was calculated according to the following equation

$$\text{combustible water recovery} = \frac{\gamma(100 - A_j)}{100(100 - A_j)} \times 100$$

where $\gamma_j$ is the yield of the concentrates; $A_i$ and $A_j$ are the ash contents of the concentrates and raw coal samples, respectively.

2.5. AFM Tests. A MultiMode 8 AFM (Bruker, Karlsruhe, Germany) was employed to observe the nanobubbles on the surface of the coal. The highly oriented pyrolytic graphite (HOPG) was used as substrate to simulate the coal surface. The nanobubbles were generated by the temperature difference method, that is, two pipes were connected to the cell for fluid replacement with 20 °C water instead of 7 °C cold water on the surface of HOPG. Meanwhile, the direct use of 20 °C water in the cell was also studied as a comparison. The measurement process of scanning the nanobubbles on the surface of the coal is described elsewhere.31 In detail, the AFM instrument was operated in the tapping mode with DNP-10 (Bruker, Karlsruhe, Germany) tip A ($k = 0.35$ N/m, $f = 65$ KHz) in a Milli-Q water environment. During the observation, the AFM instrument employed $512 \times 512$ pixel image acquisition and automatic optimization of scanning parameters (set point, feedback response, and scan rate). Before imaging, the probes were cleaned by the plasma in 3 min. The obtained images were then analyzed with NanoScope Analysis 1.5 software.

2.6. Wrap Angle Tests. Wrap angle experiment was designed to investigate particle–bubble attachment characteristics, and the experimental schematic is shown in Figure 1.

![Figure 1. Schematic diagram of wrap angle experiment.](image)

After the oxidized coal particles (2 g, 0.125–0.25 mm in size) were treated with nanobubbles and in a 20 mL plexiglass trough, a bubble (3.8 mm) was formed at the end tip of a syringe. The method of generating nanobubbles was that coal samples were placed into the cell along with water at 20 °C, which was the mixture of cold water at 7 °C and hot water at 59 °C at a ratio of 3:1. Another case is that water at 20 °C was injected into the cell. The water is Milli-Q water. After constant stirring with a magnetic rotor for 240 s, oxidized coal particles began to adhere onto the bubble surface and form the wrap angle. Testing phenomenon was recorded by a high-speed camera, and then the wrap angle was calculated.

2.7. Induction Time Tests. The coal particle–nanobubble induction time was measured using a self-constructed instrument comprising a light source, a high-speed camera (dynamic monitoring of coal particle and bubbles state), a vibration exciter (control the original bubble motion and contact time between bubbles and coal particles), a computer (control parameters), capillary, and a microsyringe (generate bubble), as shown in Figure 2. The particle size of coal was 0.125–0.25 mm. Before the test, the coal was treated with nanobubbles in the same way as in section 2.6. The coal particles formed a stationary coal particle bed on the bottom of the cell. Inside the cell, an air bubble with a diameter of approximately 3.8 mm was formed at the tip of the microsyringe before establishing contact with the coal bed. The air bubble was moved downward to coal bed for a given duration by a vibration exciter and then returned to its original position. In the test, when the contact time between the air bubble and coal was shorter than the induction time, the particles cannot attach onto the bubble, whereas there have particles on the bubble when the contact time is longer than the induction time.32 Therefore, the induction time is defined as the time that the probability of the particle attach to the bubble is 50%. To ensure statistical accuracy, ten repeated measurements were performed, and the results were reported as averages.

3. RESULTS AND DISCUSSION

3.1. Coal Characterization. The SEM results of the coal samples before and after oxidation are shown in Figure 3. Obviously, compared with fresh coal, the surface of oxidized coal is rougher. Meanwhile, element composition on the sample surface analysis indicates that the carbon content decreased from 89.34% in raw coal to 85.55% in oxidized coal, while the oxygen content increased from 7.06% in raw coal to 12.48% in oxidized coal. The contents of other elements (Si, Al, and Fe) remain virtually unchanged. These results indicate that carbonaceous substances were decreased, while oxygen-containing substances were increased after coal oxidation. Therefore, the heat effect during the oxidation process significantly changed the physicochemical properties of the coal surface.

XPS tests were carried out to further understand the surface chemical composition changes in the coal samples before and after oxidation. Figure 4 presents the wide-scan XPS spectra and reconstructed C1s peaks. As shown in the Figure 4a,b, the carbon and oxygen contents of the raw coal were 87.98 and 9.64%, and those of the oxidized coal were 82.44 and 13.24%, respectively.
respectively. It was obvious that the content of O1s on the raw coal surface was lower than that on oxidized coal. The results show that the organic components on the coal surface were oxidized and that there were oxygen-containing functional groups on the surface of the oxidized coal.

The C1s peaks and relative contents of carbon forms on the surface of the raw coal and oxidized coal are shown in Figure 4c,d. For raw coal, the spectra were fitted with four binding energy peaks at 284.64, 285.82, 286.74, and 289.34 eV, representing the C−C/C−H, C−O, C==O, and COOH groups, respectively. The proportions of the functional groups were 71.29, 10.28, 5.86, and 12.56%, respectively. For oxidized coal, the electron-binding energies were 284.48, 285.10, 286.26, and 288.78 eV, respectively. The proportions of C−C/C−H, C−O, C==O, and COOH were 60.25, 13.98, 10.05, and 15.73%, respectively. The relative content of C−C/C−H groups on the oxidized coal surface was lower than that on the raw coal surface, while the relative content of oxygen-
containing functional groups (such as C−O, C=O, and COOH) was increased on the oxidized coal surface, with a 11.04% difference. The SEM and XPS results show that oxidation changed the physical and chemical properties of the coal surface, and the content of oxygen-containing functional groups on the surface of the oxidized coal increased significantly, which would decrease the hydrophobicity of the coal samples. Therefore, the oxidized coal was difficult to float during the flotation process.

3.2. AFM Image Analysis. Figure 5 shows the HOPG surface image under different test conditions. For the HOPG surface pretreated by 20 °C Milli-Q water (Figure 5a), it could be found that its surface was very smooth. The average surface roughness was only 4 nm. However, after the HOPG surface pretreatment by the temperature difference method (Figure 5b), a large number of bright spots with sizes ranging from several to tens of nanometers appeared on the HOPG surface. What is more, the heights of these bright spots increased significantly to 12 nm. This indicated that many nanobubbles were generated on the surface of HOPG by the temperature difference method, which is in accordance with previous studies.19,31

3.3. Flotation Performance Analysis. In coal flotation, flotation dynamics is the relationship between the flotation process and time, reflecting the speed of the flotation process. The dynamic model plays an important role in guiding the industrial practice. The research on flotation dynamics mainly focuses on the changing rule of flotation rate constant k. The flotation rate constant is the flotation rate per unit time. The larger the flotation rate constant is, the faster the flotation process is.36 Based on the consistency between cleaned coal ash and cleaned coal combustible recovery, the N-order kinetic model can be expressed as follows

\[
\frac{d\varepsilon}{dt} = (\varepsilon_\infty - \varepsilon)^n
\]

where \( \varepsilon \) (%) is the cumulative combustible recovery, t (s) is flotation time, and \( \varepsilon_\infty \) (%) is theoretical maximum combustible recovery.

When \( n = 1 \), the following two traditional flotation dynamic models can be obtained:

Classical first-order model (Model 1)

\[
\varepsilon = \varepsilon_\infty (1 - e^{-kt})
\]

First-order model with rectangular (Model 2)

\[
\varepsilon = \varepsilon_\infty \left(1 - \frac{1 - e^{-kt}}{k_f t}\right)
\]

Fully mixed reactor model (Model 3) assumes that flotation components are exponentially distributed, which gives an added flexibility over the classical first-order model and enables it to fit the observed values very well. The Model 3 can be transferred into the improved gas/solid adsorption model (Model 4) by substituting \( 1/k_3 \) for \( k_4 \).

\[
\varepsilon = \varepsilon_\infty \left(1 - \frac{1}{1 + t/k_3}\right)
\]

Improved gas/solid adsorption model (Model 4)

\[
\varepsilon = \varepsilon_\infty \left(\frac{k_4 t}{1 + k_4 t}\right)
\]

With that in mind, the Model 1, Model 2, and Model 4 were chosen to study the flotation kinetic of oxidized coal in this paper, as shown in Table 1.

Table 1. Flotation Kinetics Models Used in this Paper

| Model name of the model | formula\(^a\) |
|------------------------|-------------|
| 1 classical first-order model | \( \varepsilon = \varepsilon_\infty (1 - e^{-kt}) \) |
| 2 first-order model with rectangular | \( \varepsilon = \varepsilon_\infty (1 - e^{-kt}/k_f) \) |
| 4 improved gas/solid adsorption model | \( \varepsilon = \varepsilon_\infty (k_4 t/1 + k_4 t) \) |

\( ^a \varepsilon \) is fractional recovery at time \( t \), \( \varepsilon_\infty \) is the fractional ultimate recovery, and \( k_4 \) is rate constants \( (n = 1, 2, 4) \).

Figure 6 presents the flotation results of oxidized coal in the absence and presence of nanobubbles. It was also found that the cumulative combustible recovery for oxidized coal treated with nanobubbles was significantly improved. Specially, the cumulative combustible recovery using nanobubbles is approximately 40% while that is approximately 30% in the absence of nanobubbles. Further, the data of cumulative matter recovery were fitted by Model 1, Model 2, and Model 4, respectively, as shown in Figure 6. A very good agreement between the calculated and experimental curves is obtained, which is verified by the high correlation coefficient \( R^2 \) in Table 2. The obtained correlation coefficient \( R^2 \) of Model 2 is higher than that of Model 1 and Model 4, which demonstrates that

Figure 5. AFM image of HOPG surface (a: 20 °C of Milli-Q water; b: 20 °C after mixing cold and hot water).

Figure 6. Effect of nanobubbles on the cumulative matter recovery during the oxidized coal flotation process.
the flotation process of oxidized coal in the absence and presence could be described using the first-order model with the rectangular model. As shown in Table 2, the existence of nanobubbles during the flotation process could strongly influence the fractional ultimate combustible matter recovery ($\varepsilon_{\infty}$) and the rate constant of flotation ($k$). The $\varepsilon_{\infty}$ values obtained by nanobubbles were higher than those obtained with no nanobubbles for all test models, which was in accordance with actual flotation test results. Moreover, the $k$ values obtained by nanobubbles were higher than those obtained without nanobubbles for all three kinetic models. According to Table 2, the $k$ of Model 2 increases from 3.039 to 3.431, which indicated that nanobubbles could improve the flotation rate of oxidized coal.

### 3.4. Coal–Bubble Interaction Analysis

The interaction between coal and bubble can be reflected by particle–bubble attachment, such as and wrap angle analysis and induction time analysis, which determines the flotation efficiency and performance of oxidized coal. Figure 7 shows wrap angle results of oxidized coal in the absence and presence of nanobubbles on the surface of the coal. It can be found that the existence of nanobubbles significantly increases the wrap angle of the particle–bubble from 196° to 232°, indicating that the existence of nanobubbles on the coal surface can promote more oxidized coal to adhere to the bubble. Moreover, it should be mentioned that there were some oxidized coal particle agglomeration and are observed in the Figure 7b, which was attributed to the existence of nanobubbles promoting the adhesion between coal oxide particles. This was also one of the reasons that a higher combustible matter can be obtained in the flotation process using nanobubbles pretreatment. Similarly, the induction time required for microbubble–particle attachment was 1000 ms, as shown in Figure 8. In the presence of nanobubbles, the induction time shortened to 39 ms. In general, the short induction time reflects the faster flotation rate. Therefore, a higher flotation rate was obtained when the oxidized coal surface was attached with nanobubbles.

Figure 9 describes the schematic of nanobubbles in coal flotation. For the conventional flotation (Model I), there is a direct adhesion between coal and bubble. As discussed previously, nanobubbles are preferentially generated and adsorbed on coal particle surface to enhance the hydrophobicity of coal and enlarge the hydrophobicity difference between the surface coal and ash forming mineral. After nanobubble formation on the surface of coal, nanobubbles could not only be used as bridges between coal particles (or aggregates) but also promote particle–bubble attachment, as show in Figure 9 (Model II). Then, Zhang et al. also found that nanobubbles could enhance the attachment of larger bubbles on the surface of HOPG after nanobubble formation on the surface of HOPG, which was consistent with our results. On the other hand, the aggregates could increase the apparent size of particles and increase collision probability. Therefore, nanobubbles can improve the flotation rate and efficiency of oxidized coal.

### 4. CONCLUSIONS

In this study, nanobubbles generated by the temperature difference method significantly enhanced the flotation recovery of oxidized coal. The SEM and XPS results showed that the coal surface became rough and a large number of oxygen-containing functional groups existed on the surface of the coal after oxidation, which made the oxidized coal difficult to float. AFM imaging results revealed that many nanobubbles were generated and adhesion on the oxidized coal surface via the temperature difference. Compared with conventional flotation, the combustible matter recovery of oxidized coal with nanobubbles could be increased by approximately 10%. What is more, all flotation kinetic models confirmed that coal treated with nanobubbles could obtain a higher $k$ value than the conventional flotation process. The flotation mechanism revealed that the presence of nanobubbles significantly

| Table 2. Fitted Results of Oxidized Coal Flotation in Absence and Presence of Nanobubbles |
|-------------|-----------------|--------------|-----------------|-----------------|--------------|
| model       | $\varepsilon_{\infty}$ (%) | $k$ (min$^{-1}$) | $R^2$          | $\varepsilon_{\infty}$ (%) | $k$ (min$^{-1}$) | $R^2$          |
| 1           | 32.10           | 1.441        | 0.9938         | 39.92           | 1.593        | 0.9931        |
| 2           | 35.29           | 3.039        | 0.9979         | 43.58           | 3.431        | 0.9965        |
| 3           | 37.06           | 1.819        | 0.9858         | 45.46           | 2.111        | 0.9818        |

![Figure 7](image1.png)

**Figure 7.** Results of wrap angle tests obtained for oxidized coal samples in the (a) absence and (b) presence of nanobubbles.

![Figure 8](image2.png)

**Figure 8.** Results of bubble-oxidized coal particle induction time tests.

![Figure 9](image3.png)

**Figure 9.** Schematic illustrating the role of nanobubbles in coal flotation (Model I: conventional flotation; Model II: flotation with nanobubbles pretreatment).
increased the wrap angle of oxidized coal particles from 196° to 232° and shortened the bubble-oxidized coal particle induction time from 1000 to 39 ms, promoted particle and bubble aggregation, allowing oxidized coal to be more efficiently recovered.

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