Chemical Papers (2023) 77:977–986
https://doi.org/10.1007/s11696-022-02534-0

ORIGINAL PAPER

# Development of roasting-acid leaching-magnetic separation technology for recovery of iron from “dead ores”

Long Chen[1] · Yanying He[1] · Jian Hu[1] · Qian Han[1] · Shixi Gu[1] · Pengzhang Chen[1] · Xiayan Fang[1] · Fangfang Wu[1]

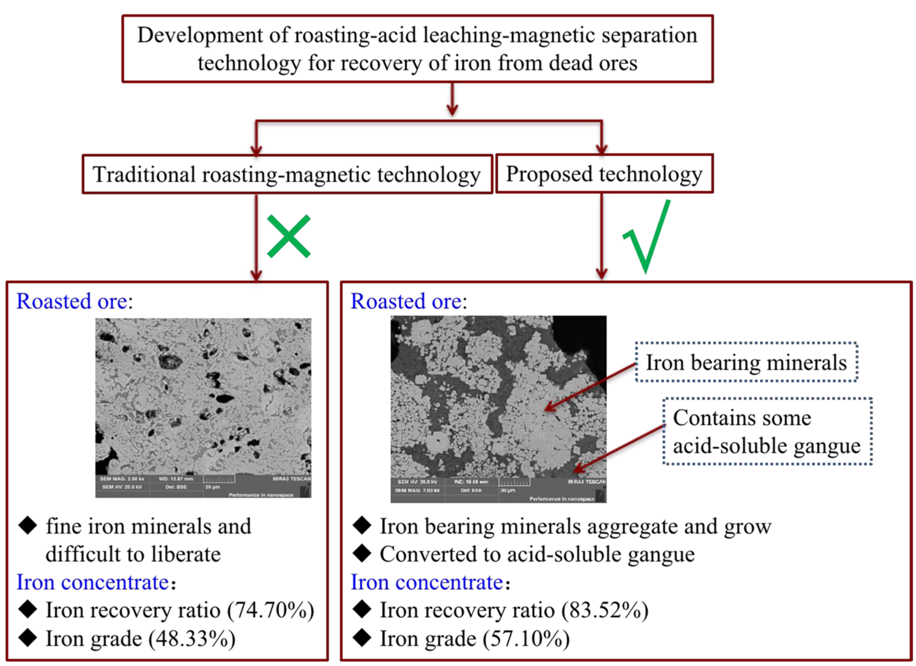
Received: 8 August 2022 / Accepted: 7 October 2022 / Published online: 16 October 2022



## Abstract

Utilization of plentiful fine-disseminated iron oxide ores resources attracted increasing attention in these years due to the depletion of easy-dressing iron ore reserves. In this paper, an improved Fe recovery method from the refractory fine-grained iron ores was proposed, and iron can be stepwise recovered by microwave-assisted reduction roasting with the addition of $Na_2SO_4$, followed by acid leaching of roasted ore and then magnetic separation of leached ore. Experimental and mechanism analysis results indicated that during the roasting process, 70.38% of $Na_2SO_4$ would react with fine-disseminated kaolinite in raw ore to form acid-soluble $NaAlSiO_4$, achieving the crude extraction of ore samples by acid leaching. Moreover, the images of SEM showed that the addition of $Na_2SO_4$ during the roasting process can also promote the aggregation and growth of iron-rich particles, promoting the iron-rich particles' liberation in milling and resulting in a further dramatic improvement in Fe grade and Fe recovery ratio of iron concentrate by magnetic separation. The iron concentrate contained 56.91% Fe, 9.48% Mn, 3.11% Al, and 1.64% Si with a recovery of 83.52%, indeed up to the iron ores quality requirement of the steel and iron industry. This technology can also provide an inspiring idea for utilizing and processing other similar raw materials.


### Graphical abstract




Long Chen and Yanying He contributed equally to this work.

Extended author information available on the last page of the article

**Keywords** Refractory iron oxide ore · Economic recycling · Fe recovery · Desilication

## Introduction

Iron ore is the primary raw material for the modern iron-smelting industry, and iron was reported to be responsible for about 95% of industrial metals (Cavaliere 2019). In recent years, the increasing demand for iron production resulted in the continual depletion of easy-dressing iron ore reserves due to long-term intemperate exploitation. This situation is much more urgent in China because most iron ores in China are low-grade and co-exist with other gangues in the form of complex mineralogy and fine grain (Chen et al. 2019; Li et al. 2016; Mao et al. 2013). Consequently, a relevantly large quantity of iron resources (nearly 1.07 billion tons in 2017 (Jégourel 2020)) long-term depends on import in consideration of higher processing costs and environmental protection problems, which significantly limits the economic and social development of China (Dong et al. 2020; Kong et al. 2019). Therefore, such conditions give rise to a continuous need to invent and develop a novel technology of refractory iron ores processing to remove co-existing gangues economically and efficiently. Fine-grained iron oxide ore is a kind of enormous refractory iron ore worldwide. Reduction roasting-magnetic separation is a common processing technique to upgrade and recover iron from this kind of iron ore, and coke/coal is the typical reducing agent used in the roasting process (Faris et al. 2017; Quast 2018; Roy et al. 2020). However, a series of environmental problems arose (Abreu et al. 2015; Liu et al. 2012; Ooi et al. 2011), especially $CO_2$ emissions (Quader et al. 2016; Ranzani da Costa et al. 2013), and the shortage of coke/coal is becoming more and more evident with the rapid growth of iron production, which has compelled to seek a renewable and environmental substitute for this traditional fossil energy.

Recently, plenty of investigations have been performed to test the reduction performance using partially or entirely replacement of coke/coal with biomass sources, such as raw biomass, charcoal, and biogas (Cheng et al. 2016; Jha and Soren 2017; Mousa et al. 2016; Solar et al. 2016; Vassilev et al. 2015; Wei et al. 2017a, 2017b), all of which concluded that biomass were kinds of effective and promising reducing agents. Besides, our previous study demonstrated a significant synergism effect between microwave heating and biomass application (alkali lignin, the main byproduct of paper-making industry) on the reducing roasting of iron oxide ores (Wu et al. 2017). Moreover, microwave technology is relatively cleaner than traditional pyrometallurgical processes, which use carbonaceous or hydrocarbon as the major energy sources, and can improve heat transfer in mineral processing (Mizuno et al. 2021; Omran et al. 2015c; Ye et al. 2019). Actually, many research reports have confirmed the advantages of microwave heating over traditional heating in iron ore processing (Nuri et al. 2014; Omran et al. 2015a, 2015b; Zhao et al. 2014). So, in these regards, microwave-assisted reduction roasting using biomass as reducing agents followed by magnetic separation seems more suitable for application in Fe recovery from refractory iron oxide ores resources.

Lanshan style iron oxide ore is a typical refractory iron resource in China, and the proven reserves exceed one billion tons, and the reserve is about 0.5 billion tons just in Lanshan County, Hunan Province. In addition, characterized by shallow burial, loose orebody and low cost of exploitation, the deposit belongs to a new-type mineral resource supported and encouraged by the Chinese government. However, due to the lack of an efficient and economical processing technique, the ore has not been effectively exploited and utilized in the past decades since its discovery, and sometimes, the resource is defined as a "dead ore" without any economic benefit. Thus, to achieve resource utilization in this area, the core of this research focused on the selective removal of gangue minerals by combing chemical and physical methods. The technical feasibility was evaluated by contrasting the separating results of traditional iron oxide ore processing method and the proposed approach. Then the separation mechanism of the novel technology was investigated by analyzing the component, phase and microstructure transformation of ore. Meanwhile, the economic benefit of preparing iron concentrate using the proposed method was also evaluated.

## Materials and methods

### Materials

The iron ore sample used in this study was collected from Lanshan County, Yongzhou City, Hunan Province. The ore sample was crushed and ground to a particle smaller than 0.25 mm (< 60 mesh) in a ball grinder. The detailed characterization of the ore sample can refer to (Wu et al. 2017). Results indicated that the ore sample is a typical fine-disseminated silicate-type iron oxide ore with 40.10% Fe, 9.40% Al, 6.92% Si, and 8.69% Mn, and goethite (FeOOH), hematite ($\alpha$-$Fe_2O_3$), jacobsite ($MnFe_2O_4$), and kaolinite ($Al_2Si_2O_5(OH)_4$) were the primary phases. Alkali lignin was purchased from Shandong Tranlin Group, China, which was used without further treatment. All the chemical reagents used in this experiment were of analytical grade.

### Experimental procedures

The proposed technology includes three steps mainly: roasting, acid leaching, and magnetic separation. The roasting process was conducted in a MAS-II microwave reactor. Firstly, 20 g ore samples were homogeneously mixed with 5% alkali lignin and/or a presetting proportion of $Na_2SO_4$, then transferred to a 100 mL corundum crucible covered with a lid. Secondly, mixed samples in a crucible were heated by microwave irradiation under optimum reduction roasting conditions obtained from our previous research (roasting temperature 200 °C, maximum microwave power 600 W and roasting time 30 min) (Wu et al. 2017). The roasting temperature is controlled by automatically regulating the microwave power output according to a feedback control signal. The corundum crucible is transparent to microwave under experimental conditions. Acid leaching experiments were carried out in a 250 mL three-neck reactor equipped with a mechanical stirrer. Unless specialized, acid leaching process was performed on the roasted ore, which was ground to 100% by being passing through a 60 mesh screen (< 0.250 mm) in advance, and the leaching conditions were controlled as: 2.0 mol/L sulfuric acid concentration, 10:1 liquid-to-solid ratio, 60 °C leaching temperature, 5 min leaching time, and 300 rpm stirring speed. After leaching, the leached solution was vacuum filtrated to obtain the solid part (leached ore), which should be further washed three times with distilled water and then dried in an oven at 70 °C. Subsequently, the dried leached ore was ground into a slurry containing 50% water in a ball mill (XMQ-150) for 8 min, and then the slurry was used for magnetic separation via Davies magnetic separator (model: XCGS-φ50) under magnetic field intensity of 160 kA/m. The Fe recovery ratio ($\varepsilon$) in the obtained product can be calculated as follow:

$$\varepsilon = (\beta \times m)/\left(\beta_0 \times m_0\right) \quad (1)$$

where $\beta$ and $\beta_0$ are Fe grades in product and raw ore, respectively; $m$ and $m_0$ are masses of products and the total mass of raw ore used for processing.

### Product analyses

Phase compositions of ore sample before and after reaction were analyzed using an X-ray diffractometer (Rigaku-TTR III), which was operated under the following conditions: Cu Kα radiation ($\lambda = 1.5418$ Å), tube voltage and the tube current of 40 kV and 250 mA, the scanning rate of 10°/min, and step size of 0.02 from 10 to 70°. After scanning, peaks in diffractograms of samples were identified by professional XRD analysis software (MDI Jade 6.5). SEM–EDX analysis was adopted to observe the dissemination characteristics and size of iron ores by scanning electron microscopy equipped with an energy dispersive spectrometer (Tescan MIRA3/Oxford X-Max20). SEM image of ore sample was obtained using back scattered-electron imaging. Before testing, the ore sample was mounted using bakelite polymer, and then the surface of the mounted sample was ground and polished by a grinding machine (Struers/Tegramin-25). Subsequently, the polished surface was treated with spray-carbon. Hysteresis loops of ore samples were measured using a vibrating sample magnetometer (VSM: Lake Shore 7410) at room temperature under a maximum magnetic field strength of about 20 kOe.

## Results and discussions

### Experiment results by traditional technology

Reduction roasting followed by a magnetic separation process was the traditional technique for iron separation. The conventional direct reduction of iron ores by coal occurs at around 1200 °C for 2–5 h, and the transformation of weak magnetic iron phases to $Fe_3O_4$/γ-$Fe_2O_3$ via reduction magnetization roasting by biomass happens at around 550 °C for 1 h (Chao et al. 2010). But the energy consumption is still higher. Referring to the advantages of microwave heating and biomass reduction in the roasting process in published literature (Nuri et al. 2014; Omran et al. 2015a, 2015b, 2015c; Wu et al. 2017; Zhao et al. 2014), the grinding fineness experiments were conducted to investigate the effect of traditional reduction roasting-magnetic separation technology on separation and recovery of ore sample under the condition of microwave heating by using alkali lignin as reducing agent. As seen in Fig. 1, 95.31% Fe recovery ratio by magnetic separation of roasted ore at a grinding fineness of 90%–74 µm was obtained, implying that iron oxides in this raw ore could be successfully magnetized via reduction roasting using alkali lignin as reducing agent, however the Fe grade of iron concentrate was only increased from 40.10% of raw ore to 47.07%. When the grinding fineness increased from 90%–74 µm to 90%–23 µm, the grade of iron concentrate only increased by 1.26% (from 47.07% to 48.33%), while the Fe recovery ratio decreased sharply might be because the particles clustered easily and hard to separate. From this, even under the ultra-fine grinding condition (90%–23 µm), the quality of the final products was still far from satisfactory for the steel and iron industry (the industrial index of Fe grade in iron ore, DZ/T 0200–2002, ≥ 56%). Therefore, it could be concluded that as for the Lanshan style iron resources, qualified iron concentrate products would

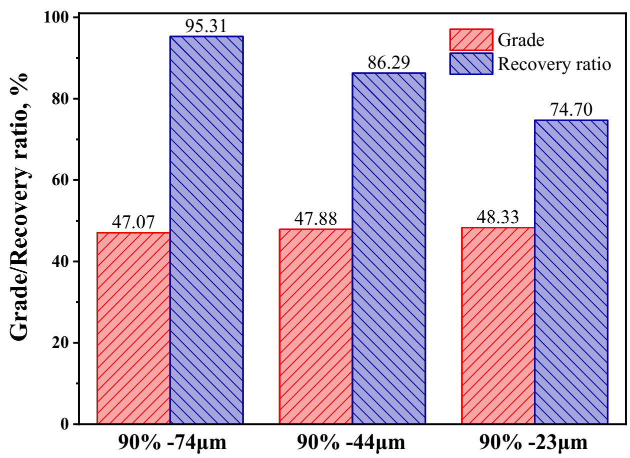



**Fig. 1** The grinding fineness experiments results

not be obtained through the traditional reduction roasting-magnetic separation method.

## Advantages of proposed technology

Quality differences of iron concentrate obtained from different experimental procedures are shown in Table 1, which indicates that although its proportion of magnetic iron oxides (including maghemite and magnetite) reached as much as 88.72% (Wu et al. 2017), traditional technology only gave iron concentrate with 48.33% Fe grade (test 5 in Table 1), while the iron concentrate grade by proposed technology was enough to meet the requirements of qualified iron concentrate product and the Fe recovery ratio remained over 70% (test 1, 2, 3). Moreover, it can be found by comparing the test results that $Na_2SO_4$ and the leaching process were beneficial in improving the Fe grade of iron concentrates, and the improvement was stepwise achieved by leaching and magnetic separation. For example, when introducing leaching process before magnetic separation, a 1% increase in Fe grade of iron concentrate was achieved, and the Fe recovery ratio of iron concentrate was also increased from 74.70 to 78.64% (test 4). Furthermore, a breakthrough improvement in the Fe grade of iron concentrate was observed combined addition of $Na_2SO_4$ with the leaching process, reaching up to 56.91% (No. 3). And compared to the results of test 3 and test 4, it can be found that 7.08% increase in the Fe grade of iron concentrate in the presence of $Na_2SO_4$ was two-step gradually achieved by leaching and magnetic separation process. Besides, it is evident from Table 1 that further enhanced the leaching conditions has almost no effect either on the Fe grade of leached ore or iron concentrate, implying that gangue in roasted ore with the addition of $Na_2SO_4$ could not be entirely selectively leached out in sulfuric acid solution, and the addition of $Na_2SO_4$ also contributes to magnetic separation.

## Mechanism analysis of proposed technology

### Effect of $Na_2SO_4$ dosage on leaching and magnetic separation

Different dosages of $Na_2SO_4$ were added during roasting processes, and the responses on the quality of leached ore and iron concentrate are shown in Fig. 2. It was found that when the dosage of $Na_2SO_4$ was below 5%, increasing the dosage of $Na_2SO_4$ resulted in a significant improvement of Fe grade of both leached ore and iron concentrate. Further increasing the dosage of $Na_2SO_4$ had no apparent effects on the Fe grade of iron concentrate, while a 2.88% Fe grade increase was still observed in leached ore by increasing $Na_2SO_4$ dosage from 5 to 10%. And the maximum Fe grade of leached ore only reached 55.08% with the addition of 10% $Na_2SO_4$, which further corroborates the conclusion obtained from results in Table 1 that acid leaching is a feasible means to selectively separate Fe-rich particles from gangue but that is relatively limited, and magnetic separation of leached ore can further enhance the effect. The quality of iron concentrate was the best with 5% $Na_2SO_4$, and Fe grade and Fe recovery ratio were 56.91 and 73.32%, respectively.

The contents of primary elements (Fe, Mn, Al, and Si) in raw ore, leached ore, and iron concentrate obtained from roasted ore with and without the addition of 5% $Na_2SO_4$ are presented in Fig. 3. Leaching ratios of four elements in roasted ores with and without 5% $Na_2SO_4$ are shown in

**Table 1** The effects of $Na_2SO_4$ and leaching process on quality of iron concentrate

| No | $Na_2SO_4$, % | Leaching parameters | Leached ores | Iron concentrates | | | |
|---|---|---|---|---|---|---|---|
| | | a $C_H$, mol/L | $t$, min | b $\beta_{Fe}$, % | c $\varepsilon_{Fe}$, % | $\beta_{Fe}$, % | $\varepsilon_{Fe}$, % |
| 1 | 5 | 0.7 | 5 | 51.24 ± 0.38 | 92.52 ± 0.63 | 57.10 ± 0.31 | 83.52 ± 0.65 |
| 2 | 5 | 0.7 | 20 | 52.77 ± 0.50 | 96.56 ± 0.44 | 56.92 ± 0.28 | 76.32 ± 0.72 |
| 3 | 5 | 2.0 | 5 | 52.20 ± 0.61 | 91.99 ± 0.94 | 56.91 ± 0.42 | 73.32 ± 1.03 |
| 4 | 0 | 2.0 | 5 | 47.97 ± 0.20 | 96.36 ± 0.25 | 49.83 ± 0.43 | 78.64 ± 1.04 |
| 5 | 0 | / | / | / | / | 48.33 ± 0.37 | 74.70 ± 0.89 |

a $C_H$: $H_2SO_4$ concentration, b $\beta_{Fe}$: Fe grade, c $\varepsilon_{Fe}$: Fe recovery.

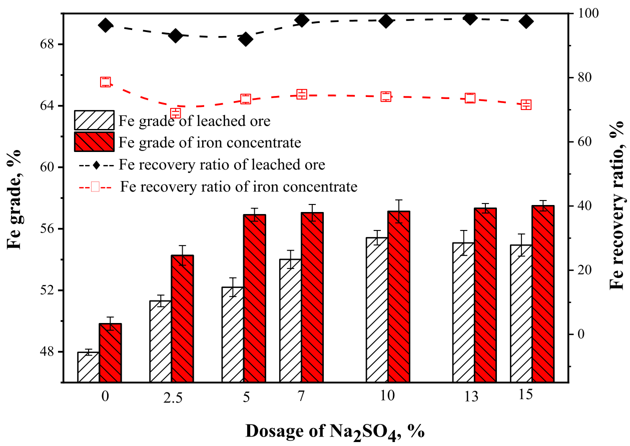



**Fig. 2** The effect of dosage of $Na_2SO_4$ on grade and recovery ratio of Fe in products

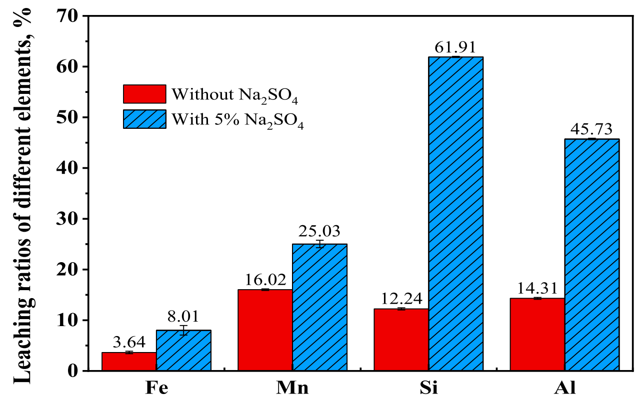



**Fig. 4** Leaching ratios of four elements in the absence and presence of 5% $Na_2SO_4$ (Leached ore products were, respectively, Leached ore 1 and Leached ore 2 shown in Fig. 3)

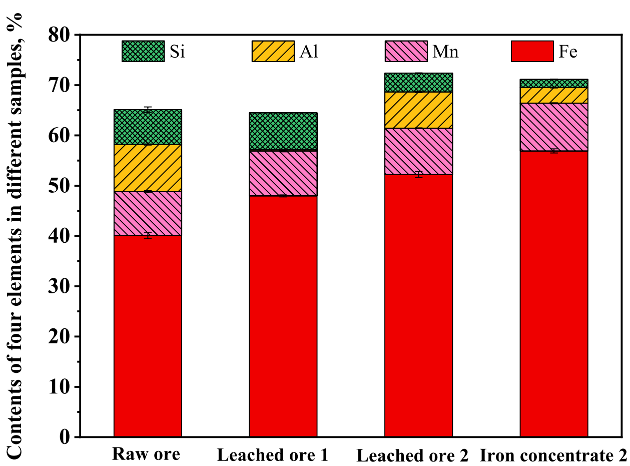



**Fig. 3** Contents of four elements in different samples (Leached ore 1 was obtained from roasted ore without $Na_2SO_4$; Leached ore 2 was from roasted ore with 5% $Na_2SO_4$; Iron concentrate 2 was from leached ore 2)

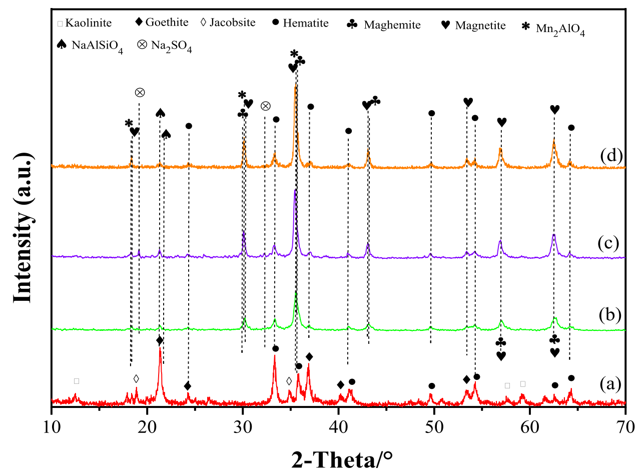



**Fig. 5** XRD patterns: **a** raw ore, **b** roasted ore without $Na_2SO_4$, **c** roasted ore with $Na_2SO_4$, **d** leached ore with $Na_2SO_4$

Fig. 4. It is obvious from Fig. 3 that the contents of Al and Si in leached ore in the presence of $Na_2SO_4$ were much lower than that in leached ore without $Na_2SO_4$, but the Mn content was slightly increased from 8.92 to 9.22%, indicating that the upgrading of Fe content in iron concentrate from 49.97 to 52.20% (shown in Table 1) with 5% $Na_2SO_4$ was attributed to the removal of Al and Si minerals. This can be further verified from Fig. 4 that the leaching ratios of Al and Si reached, respectively, 45.73 and 61.91% in the presence of 5% $Na_2SO_4$, which was almost 3.20 and 5.06 times as large as that without $Na_2SO_4$, while the leaching ratio of Fe was only increased from 3.64 to 8.01%. The iron concentrate obtained from leached ore 2 was mainly composed of Fe and Mn minerals, and the contents of Fe and Mn were 56.91 and 9.48%, respectively, while the contents of Al and Si were only 3.11 and 1.64%. The obtained iron concentrate product meets the iron ores quality requirement of the steel and iron industry (≥ 56%).

## Phase analyses

In order to reveal the phase transformation of four main elements in iron ore during roasting and leaching processes and further clear the acid-soluble phase compositions of Al and Si, XRD patterns of raw ore, roasted ores and leached ores with and without $Na_2SO_4$ are both displayed in Fig. 5. It is obvious from Fig. 5 that Fe minerals in raw ore, i.e., goethite and hematite, were reduced into magnetic iron oxides (including maghemite ($\gamma$-$Fe_2O_3$) and magnetite ($Fe_3O_4$)) in all roasted ore samples, and the presence of $Na_2SO_4$ had a significant enhanced effect on magnetic properties of roasted ore with saturation magnetization (Ms) increased

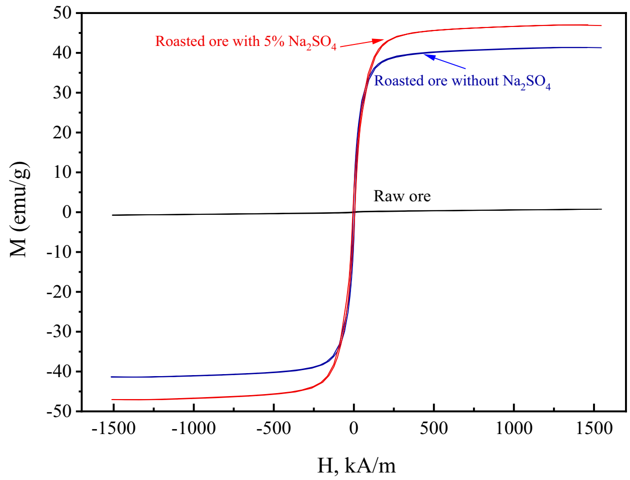



**Fig. 6** Hysteresis loops for raw ore and roasted ores with and without $Na_2SO_4$

**Table 2** Magnetic parameters for raw ore and microwave-treated ores

| Magnetic parameters | Raw ore | Roasted ores with different additives | |
|---|---|---|---|
| | | Without $Na_2SO_4$ | With 5% $Na_2SO_4$ |
| a Ms/(emu/g) | 0.75 | 41.39 | 47.22 |
| b Mr/(emu/g) | 0.10 | 5.70 | 5.38 |
| c Hc/(kA/m) | 21.10 | 4.87 | 5.35 |

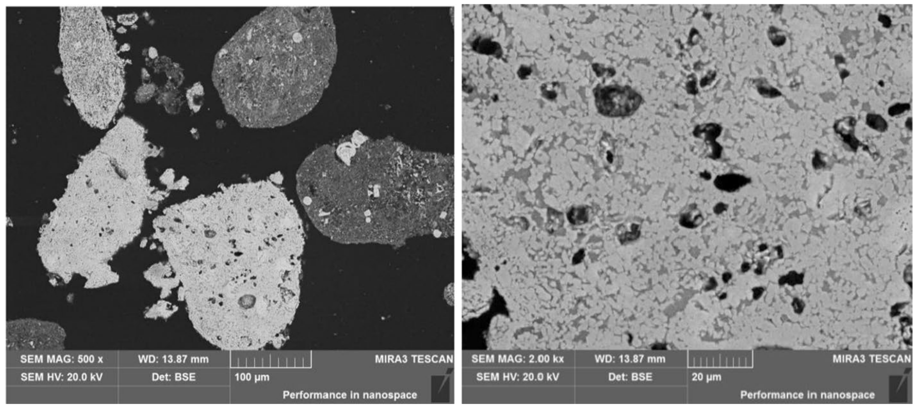
a Ms: saturation magnetization, b Mr: remanent magnetization, c Hc: coercive force.

from 41.39 to 47.21 emu/g (Fig. 6 and Table 2), which is helpful to upgrade Fe recovery ratio in iron concentrate via magnetic separation. Jacobsite ($MnFe_2O_4$) was a major Mn phase in raw ore, which was transformed into $Mn_2AlO_4$ after roasting processes, indicating dissociation of Fe from Mn in $MnFe_2O_4$ occurred. $Mn_2AlO_4$ is a kind of Mn-Al spinels, which is a more stable phase, and that may be the reason for the lower leaching ratio of Mn, as shown in Fig. 4. Al and Si in raw ore existed in the form of kaolinite. Compared the XRD results of raw ore and roasted ore without $Na_2SO_4$, it can be seen that peaks of kaolinite disappeared, and none of other Al and Si minerals were detected in roasted ore, meaning that the kaolinite phase was transformed into an amorphous aluminosilicate that could not be detected by XRD analysis. When adding 5% $Na_2SO_4$ during roasting process, peaks representing $NaAlSiO_4$ appeared, indicating that the amorphous aluminosilicate phase derived from thermal activation of kaolinite became the "nutrients" of the synthesis of $NaAlSiO_4$ phase, which was evidenced by some published studies demonstrating that kaolinite can be thermally dehydrated to amorphous metakaolin which was an activated source of Al and Si (Maia et al. 2014; Zhang et al. 2017); after leaching, the peaks of $NaAlSiO_4$ disappeared, meaning that Al and Si in roasted ore with the addition of $Na_2SO_4$ were removed in the form of $NaAlSiO_4$. Moreover, the leaching molar ratio of Al to Si with the addition of 5% $Na_2SO_4$ was about 1.04, calculated from the leaching results shown in Fig. 4, and the ratio is very close to the stoichiometric ratio of Al/Si (1:1) in $NaAlSiO_4$. The results further demonstrated that the upgrading of iron ore during acid process was mainly attributed to the removal of Al and Si phases in the form of $NaAlSiO_4$. According to the leaching ratio of Al to Si shown in Fig. 4 and the dosage of $Na_2SO_4$, it was also easily concluded that the content of $NaAlSiO_4$ in roasted ore in the presence of 5% $Na_2SO_4$ was about 21.73, and 70.38% of added $Na_2SO_4$ was an ingredient in the production of $NaAlSiO_4$.

## Microstructure analyses

Dissemination characteristic of iron grains is extremely essential for the quality of iron concentrate obtained via magnetic separation due to the insufficient iron minerals liberation from gangue in milling if the sizes of iron grains are too small (Gualtieri and Bellotto 1998; Maia et al. 2014). For instance, although the Ms of raw iron ore after roasting with the addition of 5% alkali lignin has increased from 0.745 to 41.39 emu/g (Fig. 6), which resulted in a good Fe recovery ratio of iron concentrate (74.70% as shown in Table 1), while the Fe grade of iron concentrate only reached 48.33%, far below the industrial index of iron ores used in steel and iron industry (≥ 56%). This was attributed to the fine granule distribution of iron particles in the matrix of gangue shown in Fig. 7. The particle size of roasted ore with 5% $Na_2SO_4$ was significantly larger than the feed ore sample (0.25 mm), and roasted ore was in a sleek profile as showed in Fig. 8a. The phenomenon indicated that using $Na_2SO_4$ as an additive can form substances with a low melting point in roasted iron ore during the roasting process. It is worth mentioning that the existence of low melting point material plays an important role in the gathering and growth of iron-rich particles, which can facilitate the separation and recovery of iron ore by physical methods. As noted above, in roasted ore with the addition of 5% $Na_2SO_4$, significant sintering phenomenon and agglomeration of iron-rich particles were significantly observed, and the iron-rich particles even grew into larger granular structures. That may be the reason for a sharp increase in Fe grade in the presence of 5% $Na_2SO_4$ after magnetic separation from 52.20% of leached ore to 56.91% of iron concentrate, while the value-added without $Na_2SO_4$ was only 1.86% (test 3 and 4 in Table 1). Moreover, significant intergranular fractures between iron minerals were formed after roasting, which could be attributed to the selective heating of microwave irradiation. Many literature studies also have reported the application

**Fig. 7** SEM images of roasted ore without $Na_2SO_4$ (iron-rich particles: white areas; gangue: gray areas)



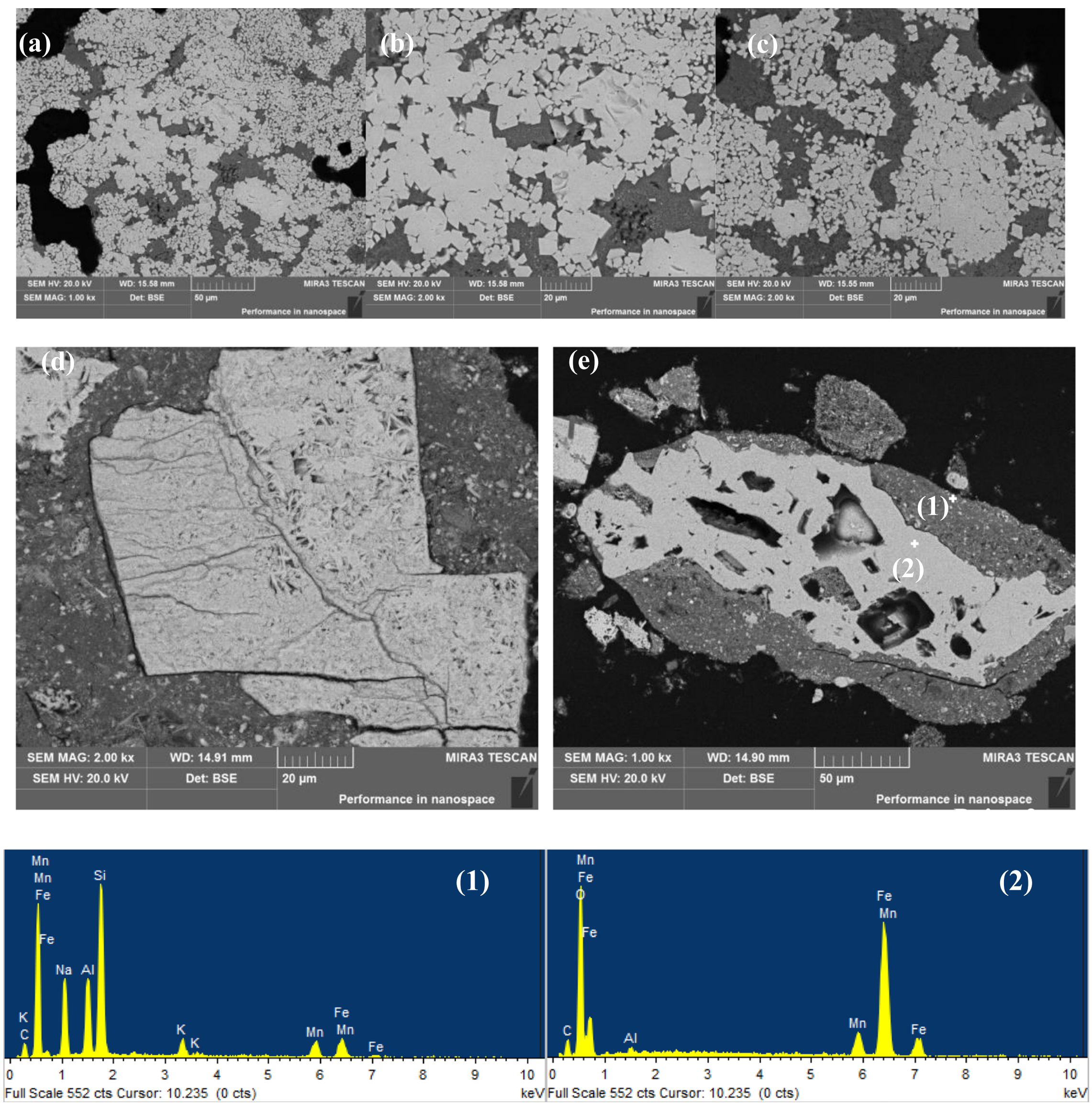




**Fig. 8** SEM images of roasted ore with 5% $Na_2SO_4$, and EDS results of (1) and (2) (iron-rich particles: white areas; gangue: gray areas)

of microwave-assisted grinding due to the crack formation in the gangue matrix (Kumar et al. 2010; Omran et al. 2015b). Thus, the aggregation and growth of iron minerals and the formation of intergranular fractures were jointly conducive to improving the magnetization effect of iron oxides in raw ore, which was in accordance with the highest value of Ms with $Na_2SO_4$ (Fig. 6), and also promoted iron-rich particles liberated in milling, decreased the cost of milling, upgraded the Fe grade and the Fe recovery ratio of iron concentrate.

### Economic and environmental assessment

Based on the above results and discussion, a qualified iron concentrate cannot be obtained through the traditional method and yet the selective removal of gangue was achieved by the proposed novel technology. Its innovations and notable merits lie in that: (1) The reduction temperature has been decreased from 550 to 1200 °C (Chao et al. 2010) to 200 °C, which can significantly reduce the energy consumption during the roasting process; (2) For refractory fine-grained iron oxide ores, traditional reduction roasting-magnetic separation process often requires multi-stage grinding ore to realize the liberation of iron grains. The overall process consumes much energy. Moreover, this technique is complex and ore dependent. It does not work for some refractory fine-grained low-grade iron oxide ores like Lanshan style iron ore. However, by using the proposed technology, the grinding process before magnetic separation was only one time; (3) Biomass resource (alkali lignin, a byproduct of paper-making) was used as a reducing agent during roasting process instead of coke/coal, meeting the development direction of environment-friendly energy sources; (4) Much like other extractive resources, the quality of iron ore is a determining factor of its price (Jégourel 2020). The raw ore was considered to have no potential value in industrial applications. The price of iron concentrate recovered from the raw ore through this novel technology is about 600 RMB/t. In addition, the content of Mn in ion concentrate was over 9%, meaning that the price could be higher. More importantly, the yield of qualified iron concentrate after implementing the technology could reach 58.65%. Generally, the increment economic benefits of the raw ore's output value can be estimated as follows: yield × unit price = 58.65% × 600 RMB/t = 351.92 RMB/t.

Coke/coal is the typical reducing agent in traditional reduction roasting process. However, a series of environmental problems arose, especially $CO_2$ emissions, and the shortage of coke/coal is becoming more and more evident with the rapid growth of iron production. Biomass has been proven to be an effective and cleaner reducing agent during the roasting process. And $Na_2SO_4$ is also a typical additive used in direct reduction roasting process with a small environmental risk (Jiang et al. 2013; Rao et al. 2015). Besides, our previous study demonstrated to a significant environmental risk reduction by microwave heating and biomass application (alkali lignin) in the reduction roasting of iron oxide ores (Wu et al. 2017). Above all, the proposed technology has cost and environmental protection advantages.

## Conclusions

In this paper, $Na_2SO_4$ was innovatively introduced into the magnetization-roasting process of iron oxide ores, and proposed an efficient three-step upgrading method for refractory fine-grained iron oxide ores, including microwave-assisted roasting, followed by acid leaching of roasted ore and then magnetic separation of leached ore. The effect of $Na_2SO_4$ on the proposed technology was investigated in terms of composition, phase and microstructure transformations of iron ore sample. Results indicated that Si and Al minerals in ore were partly selectively removed by the acid leaching process in the form of $NaAlSiO_4$ synthesized from $Na_2SO_4$ and thermal activated kaolinite. When adding 5% $Na_2SO_4$, the content of $NaAlSiO_4$ in roasted ore was about 21.73%, consuming about 70.38% of added $Na_2SO_4$ and with leaching ratios of Al for 45.73% and Si for 61.91%, respectively. $Na_2SO_4$ can also promote the aggregation and growth of iron minerals, thus increasing the iron minerals liberation and upgrading the Fe grade of iron concentrate. Formation of intergranular fractures between iron minerals and gangue in roasted ore attributed to selective heating by microwave irradiation can decrease the power consumption of milling before magnetic separation. Qualified iron concentrate (56.91% Fe) with a higher recovery ratio (83.52%) can be produced through this proposed technology with the advantages of cost-saving and environmental protection.

**Acknowledgements** This work was supported by Hunan Province Science and Technology Talent Support Project [Grant number 2022TJ-N15]; Key scientific research project of Education Department of Hunan Province [Grant number 20A245]; General project of Natural Science Foundation of Hunan Province [Grant number 2021JJ30410]; General project of Natural Science Foundation of Hunan Province [Grant number 2022JJ30348]; China postdoctoral science foundation [Grant number 2018M640750].

**Author contributions** L Chen: Conceptualization, Methodology, Formal analysis, Writing—review & editing, Funding acquisition; Y He: Investigation, Data curation, Validation, Writing—original draft; J Hu: Investigation, Data curation, Formal analysis; Q Han: Investigation, Data curation; S Gu: Conceptualization, Data curation; P Chen: Conceptualization, Methodology, Supervision; X Fang: Resources, Supervision; F Wu: Resources, Funding acquisition, Methodology, Supervision, Validation.

**Funding** Hunan Province Science and Technology Talent Support Project, 2022TJ-N15, Fangfang Wu, Key scientific research project of Education Department of Hunan Province, 20A245, Fangfang Wu, Natural science foundation of Hunan province, 2021JJ30410, Fangfang

Wu, Natural Science Foundation of Hunan Province, 2022JJ30348, Fangfang Wu, China postdoctoral science foundation, 2018M640750, Fangfang Wu.

## Declarations

**Conflict of interests** The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## References

Abreu GC, Carvalho JAd, Silva BECd, Pedrini RH (2015) Operational and environmental assessment on the use of charcoal in iron ore sinter production. J Cleaner Prod 101:387–394

Cavaliere P (2019) Sintering: most efficient technologies for greenhouse emissions abatement. In: Cavaliere P (ed) Clean ironmaking and steelmaking processes: efficient technologies for greenhouse emissions abatement. Springer Internationa Publishing, Cham, pp 111–165

Chen P, Hou P, Zhai J, Sun W (2019) A novel method for the comprehensive utilization of iron and titanium resources from a refractory ore. Sep Purif Technol 226:1–7

Cheng Z, Yang J, Zhou L, Liu Y, Guo Z, Wang Q (2016) Experimental study of commercial charcoal as alternative fuel for coke breeze in iron ore sintering process. Energy Convers Manage 125:254–263

Dong D, Espinoza LAT, Loibl A, Pfaff M, Tukker A, Van der Voet E (2020) Scenarios for anthropogenic copper demand and supply in China: implications of a scrap import ban and a circular economy transition. Resour Conserv Recycl 161:104943

Faris N, Tardio J, Ram R, Bhargava S, Pownceby MI (2017) Investigation into coal-based magnetizing roasting of an iron-rich rare earth ore and the associated mineralogical transformations. Miner Eng 114:37–49

Gualtieri A, Bellotto M (1998) Modelling the structure of the metastable phases in the reaction sequence kaolinite-mullite by X-ray scattering experiments. Phys Chem Miner 25(6):442–452

Jégourel Y (2020) The global iron ore market: From cyclical developments to potential structural changes. Extr Ind Soc 7(3):1128–1134

Jha G, Soren S (2017) Study on applicability of biomass in iron ore sintering process. Renew Sustain Energy Rev 80:399–407

Jiang M, Sun T, Liu Z, Kou J, Liu N, Zhang S (2013) Mechanism of sodium sulfate in promoting selective reduction of nickel laterite ore during reduction roasting process. Int J Miner Process 123:32–38

Kong Z, Dong X, Jiang Q (2019) Forecasting the development of China's coal-to-liquid industry under security, economic and environmental constraints. Energy Econ 80:253–266

Kumar P, Sahoo BK, De S, Kar DD, Chakraborty S, Meikap BC (2010) Iron ore grindability improvement by microwave pre-treatment. J Ind Eng Chem 16(5):805–812

Li C, Sun H, Bai J, Li L (2010) Innovative methodology for comprehensive utilization of iron ore tailings: Part 1 the recovery of iron from iron ore tailings using magnetic separation after magnetizing roasting. J Hazard Mater 174(1–3):71–77

Li W, Liu Z, Huang Q, Tang Y, Qiu X (2016) Extraction of low-grade silver from a refractory Au-Ag ore in cyanidation by pretreatment with reductive alkaline leaching. Hydrometallurgy 164:257–264

Liu G, Zheng M, Du B, Nie Z, Zhang B, Liu W, Li C, Hu J (2012) Atmospheric emission of polychlorinated naphthalenes from iron ore sintering processes. Chemosphere 89(4):467–472

Maia AÁB, Angélica RS, de Freitas NR, Pöllmann H, Straub C, Saalwächter K (2014) Use of 29Si and 27Al MAS NMR to study thermal activation of kaolinites from Brazilian Amazon kaolin wastes. Appl Clay Sci 87:189–196

Mao Z, Cheng Y, Liu J, Yuan S, Wu S, Xiang X, Luo X (2013) Geology and molybdenite Re–Os age of the Dahutang granite-related veinlets-disseminated tungsten ore field in the Jiangxin Province, China. Ore Geol Rev 53:422–433

Mizuno N, Kosai S, Yamasue E (2021) Microwave-Based Approach to Recovering Zinc from Electric Arc Furnace Dust Using Silicon Powder as a Non-carbonaceous Reductant. JOM 73(6):1828–1835

Mousa E, Wang C, Riesbeck J, Larsson M (2016) Biomass applications in iron and steel industry: an overview of challenges and opportunities. Renew Sustain Energy Rev 65:1247–1266

Nuri OS, Mehdilo A, Irannajad M (2014) Influence of microwave irradiation on ilmenite surface properties. Appl Surf Sci 311:27–32

Omran M, Fabritius T, Elmahdy AM, Abdel-Khalek NA, El-Aref M, Elmanawi AE-H (2015a) XPS and FTIR spectroscopic study on microwave treated high phosphorus iron ore. Appl Surf Sci 345:127–140

Omran M, Fabritius T, Elmahdy AM, Abdel-Khalek NA, Gornostayev S (2015b) Improvement of phosphorus removal from iron ore using combined microwave pretreatment and ultrasonic treatment. Sep Purif Technol 156:724–737

Omran M, Fabritius T, Mattila R (2015c) Thermally assisted liberation of high phosphorus oolitic iron ore: a comparison between microwave and conventional furnaces. Powder Technol 269:7–14

Ooi TC, Thompson D, Anderson DR, Fisher R, Fray T, Zandi M (2011) The effect of charcoal combustion on iron-ore sintering performance and emission of persistent organic pollutants. Combust Flame 158(5):979–987

Quader MA, Ahmed S, Raja Ghazilla RA, Ahmed S, Dahari M (2016) Evaluation of criteria for CO2 capture and storage in the iron and steel industry using the 2-tuple DEMATEL technique. J Cleaner Prod 120:207–220

Quast K (2018) A review on the characterisation and processing of oolitic iron ores. Miner Eng 126:89–100

Ranzani da Costa A, Wagner D, Patisson F (2013) Modelling a new, low $CO_2$ emissions, hydrogen steelmaking process. J Cleaner Prod 46:27–35

Rao M, Ouyang C, Li G, Zhang S, Zhang Y, Jiang T (2015) Behavior of phosphorus during the carbothermic reduction of phosphorus-rich oolitic hematite ore in the presence of $Na_2SO_4$. Int J Miner Process 143:72–79

Roy SK, Nayak D, Rath SS (2020) A review on the enrichment of iron values of low-grade Iron ore resources using reduction roasting-magnetic separation. Powder Technol 367:796–808

Solar J, de Marco I, Caballero BM, Lopez-Urionabarrenechea A, Rodriguez N, Agirre I, Adrados A (2016) Influence of temperature and residence time in the pyrolysis of woody biomass waste in a continuous screw reactor. Biomass Bioenergy 95:416–423

Vassilev SV, Vassileva CG, Vassilev VS (2015) Advantages and disadvantages of composition and properties of biomass in comparison with coal: an overview. Fuel 158:330–350

Wei R, Feng S, Long H, Li J, Yuan Z, Cang D, Xu C (2017a) Coupled biomass (lignin) gasification and iron ore reduction: a novel approach for biomass conversion and application. Energy 140:406–414

Wei R, Zhang L, Cang D, Li J, Li X, Xu CC (2017b) Current status and potential of biomass utilization in ferrous metallurgical industry. Renew Sustain Energy Rev 68:511–524

Wu F, Cao Z, Wang S, Zhong H (2017) Phase transformation of iron in limonite ore by microwave roasting with addition of alkali lignin and its effects on magnetic separation. J Alloys Compd 722:651–661

Ye Q, Li G, Peng Z, Lee J, Lin X, Rao M, Zhang Y, Jiang T (2019) Microwave-assisted self-reduction of composite briquettes of zinc ferrite and carbonaceous materials. Powder Technol 342:224–232

Zhang K, Xl C, Wc G, Hj L, Zj G, Li Bw Wu, Wf, (2017) Effects of biomass reducing agent on magnetic properties and phase transformation of Baotou low-grade limonite during magnetizing-roasting. PLoS ONE 12(10):e0186274

Zhao W, Chen J, Chang X, Guo S, Srinivasakannan C, Chen G, Peng J (2014) Effect of microwave irradiation on selective heating behavior and magnetic separation characteristics of Panzhihua ilmenite. Appl Surf Sci 300:171–177

**Publisher's Note** Springer Nature remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.



## Authors and Affiliations

**Long Chen[1] · Yanying He[1] · Jian Hu[1] · Qian Han[1] · Shixi Gu[1] · Pengzhang Chen[1] · Xiayan Fang[1] · Fangfang Wu[1]**

✉ Fangfang Wu
wufangfang@hunau.edu.cn

[1] School of Chemistry and Materials Science, Hunan Agricultural University, Changsha 410128, Hunan, People’s Republic of China