Hydrothermal Monodisperse Microspherulite Pyrite: Novel Synthesis Process and Electrochemical Study of Its Oxidation

Lin Li* and Ahmad Ghahreman*

ABSTRACT: A simple one-step hydrothermal method was developed to synthesize pyrite (FeS₂) sheet- and bulklike pyrite mineral. The Fe/S molar ratio determines the phase of FeS₂, including pyrite and marcasite. The reaction temperature and time are key factors to regulate the structure, morphology, and size of pyrite. Scanning electron and transmission electron microscopy showed the formation of monodisperse microspherulite within 1 h reaction time, and the particles aggregated to large irregular polyhedron particles with increasing reaction time up to 4 h. Electrochemical oxidation tests demonstrated that their electrochemical activity significantly decreased with increasing synthesis time. At an elevated temperature of 200 °C, bulk pyrite was obtained after a 24 h reaction time, which could have promising applications in hydrothermal pyrite ore oxidation research.

1. INTRODUCTION

Pyrite (FeS₂), the most abundant sulfide mineral in the earth’s crust, is a semiconductor mineral commonly associated with metal (Au, Cu) and coal deposits. Pyrite is a major source of acid mine drainage (AMD), which causes serious environmental issues at mining sites worldwide, especially given that pyrite-beariing ore is an important host for toxic elements like arsenic, cadmium, cobalt, chromium, and mercury. Due to its low fabrication cost and high electric power conversion efficiencies, pyrite has become a promising semiconductor material for photovoltaic solar cells, which directly convert solar energy into electricity. Other novel applications of pyrite include cathode materials for lithium-ion batteries and catalysts for clean energy H₂ production. Pyrite oxidation also attracts research attention because pretreatment of refractory gold-bearing pyrite ore is essential to improving gold leaching efficiency.

These environmental concerns and the broad suite of potential applications have led to an interest in pyrite properties. For instance, pyrite oxidation kinetics is of utmost importance in AMD. Oxidation rates differ for pyrite originating from different locations, which has been attributed to trace and minor elements in natural pyrite that change the semiconducting properties and hence the conductivity and surface states of pyrite. In addition, the semiconducting properties of pyrite have been linked to the precise composition (purity elements) of the pyrite sample.

Various methods to enhance the performance of pyrite have been extensively studied. For instance, cobalt doping can improve visible light absorption, leading to better photocatalytic performance. However, the effects of impurities, which are commonly found in natural pyrite, on pyrite oxidation are poorly understood. Synthesizing pyrite and then doping it with a single element is a simple and low-cost approach to study the effect of an impurity on pyrite oxidation. However, the synthetic pyrite should be similar to natural pyrite, that is, it should be bulk pyrite or have a large particle size, vs the pyrite nanoparticles often presented in the material science research.

Among the available methods to synthesize pyrite (e.g., electrodeposition, chemical bath deposition, chemical vapor deposition, thermal sulfurization, and hydrothermal methods), hydrothermal methods are the most simple and cost-effective. They are most suitable for production of bulk pyrite with a uniform structure, which is applicable for AMD and hydrometallurgical research. However, two drawbacks to the hydrothermal methods are: (1) the synthetic pyrite has various mineral shapes, which can limit its applicability; and (2) elemental sulfur forms as a byproduct. For example, marcasite is FeS₂ that has a similar lattice structure to pyrite. Although the pyrite cubic lattice structure is composed of a center-facing Fe atom, octahedrally coordinated by six S atoms (Figure 1a), marcasite consists of linear chains of edge-sharing S₂²⁻ octahedra (Figure 1b). Compared to pyrite, marcasite has a much smaller band gap (0.34 eV), which is believed to impede...
the photovoltaic performance when marcasite is mixed with pyrite.\(^3\)\(^1\) Pyrite is more inert to oxidation than marcasite.\(^3\)\(^1\)

Carbon disulfide (CS\(_2\))—by far the most efficient sulfur solvent—has been widely used to remove sulfur from pyrite through solvent extraction; it exhibits a sulfur solubility of 35.5 g in 100 g CS\(_2\) at 25 °C.\(^3\)\(^2\) However, CS\(_2\) is highly neurotoxic.\(^3\)\(^3\) Toluene is far less toxic than CS\(_2\), and sulfur is highly soluble in hot toluene (11.56 g in 100 g toluene at 80 °C).\(^3\)\(^4\)

This study develops a novel, one-step, hydrothermal process to synthesize pyrite as monodisperse microspherulites and large irregular polyhedron particles. Knowing that sulfur solubility in organic solvents increases with temperature,\(^3\)\(^4\) we also developed a process to use toluene, as an alternative of the common use of CS\(_2\), for elemental sulfur removal from synthetic pyrite at elevated temperature. The reaction occurs in aqueous solution with inorganic Fe and S sources, and no surfactant is used. Electrochemical tests were conducted to measure the oxidation rates and semiconducting properties of pyrite synthesized over different time periods, which provides insights on the leaching behavior of hydrothermally formed natural pyrite.

2. RESULTS

2.1. Effect of Fe/S Molar Ratio on Pyrite Synthesis. X-ray diffraction (XRD) patterns of the impure synthetic pyrite at a Fe/S ratio of 1:4 (Figure 2a) confirm the formation of elemental sulfur (PDF #08-0247) and pyrite (PDF #42-1340). The application of toluene as an alternative to CS\(_2\) for sulfur removal was very effective: It completely removed the sulfur from the final products. After sulfur removal, no peaks of elemental sulfur were detected in the XRD patterns (Figure 2b).

When Fe/S was 1:1, high-intensity peaks of marcasite (PDF #37-0475) were found (Figure 2b). Increasing the source S concentration (Fe/S = 1:2) significantly decreased the intensities of the character peaks of marcasite. The effect of the molar ratio of Fe/S has been affirmed in determining the iron sulfide phase. In the following tests in this study, the molar ratio Fe/S of 1:4 was used to fabricate pure pyrite. All subsequent experiments used pure-phase pyrite after purification.

2.2. Effect of Reaction Time on Pyrite Synthesis. XRD peaks of pyrite products from 1, 2, and 4 h of synthesis (Figure 3a) correspond to a pyrite crystal structure (JCPDS No. 42-1340). No impurity peaks were detected. Particle size increased with reaction time (Figure 3b): Mean particle sizes were 32, 60, and 108 μm for pyrite produced in 1, 2, and 4 h, respectively. This suggests a possible aggregation-based mechanism. Pyrite synthesized in 1 h had the narrowest particle size distribution, whereas pyrite synthesized in 2 h had two recognizable fractions: 40–80 and 80–150 μm (Figure 3b).

All of the synthetic and natural pyrite only started to lose weight from about 180 °C (Figure 3c). In the first stage (180–600 °C), the pyrolysis of pyrite progressed\(^3\)\(^5\)
\[
\text{FeS}_2(s) \rightarrow \text{FeS}_{1-x}(s) + \frac{(1 - x)}{2} \text{S}_2(g)
\]
(1)

According to the reaction, pyrrhotite and sulfur could be produced during pyrolysis. Compared to natural pyrite, synthetic pyrite tends to lose sulfur more easily in this temperature range. Both natural and synthetic pyrite began to severely decompose at 600 °C (Figure 3c). The reaction of this second stage can be written as\(^3\)\(^5\)
\[
\text{FeS}_2(s) \rightarrow \text{FeS}(s) + \frac{1}{2} \text{S}_2(g)
\]
(2)

Natural pyrite lost 22.5% of the initial sample weight at 800 °C, vs approximately 27% for the three synthetic pyrites (Figure 3c). The pyrite synthesized in 2 and 4 h has a slightly higher thermal resistance than the pyrite synthesized in 1 h.

Pyrite synthesized in 1 h showed several microspheres (Figure 4a), some well dispersed and others are in the process of merging into larger amorphous particles. The particle size of this pyrite is 2–10 μm (Figure 4a). By comparison, pyrite particles synthesized over 4 h had irregular shapes (Figure 4b), which is likely due to intensive aggregation with increasing reaction time. Scanning electron microscopy (SEM) images of whole particles showed discernible agglomeration of particles into
spherical and polyhedral shapes for pyrite synthesized over 1 h (Figure 4c) and 4 h (Figure 4d), respectively.

A high-magnification transmission electron microscopy (TEM) image of pyrite synthesized in 4 h shows several small, irregularly shaped nanoparticles, some assembled into larger irregular polyhedral particles (Figure 5a). The fringe spacing value was determined to be 0.271 nm (Figure 5b), corresponding to a lattice spacing of (200) plane of pyrite (JCPDS #042-1340). The selected-area electron diffraction pattern displays (2 2 0), (2 0 1), and (2 0 0) planes indexed for pyrite diffraction patterns (Figure 5c). The bright and clearly observed spots in the pattern reveal the highly crystallized polyhedron.

2.3. Electrochemical Study. Pyrite oxidation is essentially an electrochemical process; the oxidation rate is influenced by the electrical conductivity. The conductivity of the pyrite synthesized in 4 h initially increased with applied pressure and became stable after approximately 310 kPa (Figure 6). At this pressure, the conductivities of pyrite synthesized in 1, 2, and 4 h were 3.85, 12.5, and 14.3 S/cm. These results agree with other work showing that increasing grain size—or decreasing grain boundary—and increasing crystallinity significantly reduced the resistivity of polycrystalline semiconductor films.

The electrochemical oxidation behavior for pyrite synthesized for the three reaction times was evaluated in terms of the relationship between the logarithm of current density and applied potential (Figure 7). The exchange current density ($i_0$)—a measure of electrochemical activity—was highest for pyrite synthesized in 1 h and lowest for pyrite synthesized in 4 h (Table 1). These data suggest that the relatively small particle size (Figure 7) and thus a large surface area-to-volume ratio of pyrite synthesized in 1 h are the mechanisms behind the high electrochemical activity.

To further analyze the semiconductor properties of the synthetic pyrite, Mott–Schottky tests were conducted. Mott–Schottky curves for the three pyrite samples have two distinct linear regions before and after 0.6 V (Figure 10). A similar phenomenon has been reported for n-type semiconductors with
a depletion region.39 The positive slope at a potential less than 0.6 V could be explained by the pseudo-passive behavior of pyrite in sulfuric acid solution. At potentials above 0.6 V, reaction 3 generated new products and changed the surface properties.40 Clearly, synthesis time, especially longer than 2 h, affected the semiconducting properties (Figure 8), which could subsequently affect the electrochemical oxidation behavior.

Fe$_{1-x}$S$_2$ + 8H$_2$O $\rightarrow (1-x)$Fe$^{3+} + 2$HSO$_4^- + 14$H$^+$ + 3(5 - x)e$^-$ (3)

2.4. Synthesis of Bulk Pyrite. The results above show that synthetic pyrite has a strong tendency to aggregate with extended synthesis time. Temperature also plays a key role in morphological control in the hydrothermal reaction.23 At 180 °C, the products displayed a laminar, sheetlike structure that was thicker at longer reaction times (Figure 9, top). At 200 °C, the pyrite synthesized in 4 h comprised a rough layer; at 12 h, the pyrite was “chunkier,” and at 24 h, the pyrite was aggregated into large chunks with a smooth surface (Figure 9, bottom). The surface of the bulk pyrite had several pits, possibly due to the evaporation of elemental sulfur on the surface at high temperatures and pressures. The SEM graph for the pyrite synthesized at 200 °C at 24 h showed complete irregular particle shape with a larger size range from several to 50 μm.

In the Fe 2p spectra, the highest-intensity peak at 701.1 eV is FeS$_2$.41 (Figure 10a). A peak at 711.5 eV in bulk pyrite (Figure 10b), which has not been previously observed, is ferric oxide. The peaks differ because sheetlike pyrite has a more active surface to host ferrous oxidation. S 2p peaks usually give rise to doublets of S 2p$_{3/2}$ and S 2p$_{1/2}$ owing to spin−orbit splitting.42 For clarity, the S 2p spectra only present S 2p$_{3/2}$ peaks of fitted curves in Figure 10c,d. The peaks of S 2p at 162.5, 163.4, and 168.5 eV correspond to sulfide, polysulfide, and sulfate, respectively.43 The percentage of polysulfides was higher in bulk pyrite (16.91%) than in sheetlike pyrite (7.64%; Figure 10e). On the other hand, the percentage of sulfate was higher for sheetlike pyrite (25.70%) than for bulk pyrite (11.46%), which suggests different degrees of oxidation and a possible two-step oxidation mechanism.

3. DISCUSSION

3.1. Pyrite Synthesis and Characterization. To preferentially control the morphology and purity of the pyrite as a functional material, organic Fe and S sources were normally used. However, the raw material can be costly, and the synthesis condition is not suitable for large-scale production, especially for hydrometallurgical and geochemical research. In this study, inexpensive inorganic iron and sulfur sources, FeSO$_4$ and Na$_2$SO$_3$, were used to synthesize pyrite via a one-step hydrothermal method.

Pyrite was synthesized at different molar ratios of Fe/S sources, 1:1, 1:2, and 1:4, at 180 °C for 4 h. The XRD analysis (Figure 4) proved the Fe/S molar ratio acted as a vital factor for the iron sulfide phase in the products. The identification of marcasite was detected for the products at Fe/S ratios of 1:1 and

![Figure 5](https://dx.doi.org/10.1021/acsomega.0c03613)

Pyrite nanoparticles synthesized over 4 h: (a) high-magnification TEM image, (b) high-resolution TEM image, and (c) selected-area electron diffraction pattern.

![Figure 6](https://dx.doi.org/10.1021/acsomega.0c03613)

Conductivity of pyrite synthesized in 4 h vs applied pressure.

![Figure 7](https://dx.doi.org/10.1021/acsomega.0c03613)

Tafel plots for the synthetic pyrite oxidation in 0.5 M sulfuric acid solutions.

| pyrite synthesis time (h) | $i_0$ ($10^{-6}$ A/cm$^2$) | $E^0$ (V) | $\alpha_1$ | $\alpha_2$ | n  |
|--------------------------|--------------------------|----------|-----------|-----------|----|
| 1                        | 1.58                     | 0.44     | 0.44      | 0.51      | 0.96 |
| 2                        | 5.62                     | 0.42     | 0.33      | 0.59      | 0.92 |
| 4                        | 9.12                     | 0.40     | 0.17      | 0.78      | 0.95 |

Table 1. Kinetics Parameters Determined by Tafel Analysis
1:2 (Figure 4b), and the intensity peaks for marcasite reduced sharply for the Fe/S ratio of 1:2. For the Fe/S ratio of 1:4, the peak intensity of the marcasite phase disappeared completely, leaving pyrite as the only iron sulfide phase together with elemental sulfur (Figure 4a). The probable reaction happened as

$$\text{FeSO}_4 + 4\text{Na}_2\text{S}_2\text{O}_3 \rightarrow \text{FeS}_2 + 4\text{Na}_2\text{SO}_4 + 3\text{S}$$

(4)

To separate the pyrite from the pyrite-sulfur mix and recycle the elemental sulfur, the toluene solvothermal method was designed to dissolve the elemental sulfur and obtain pure-phase pyrite. Conventional sulfur purification methods include the annealing process44 or the organic solvent extraction method.45 A post-annealing process at high temperatures has high energy consumption and consequently modifies the original characters of the products. Organic solvents such as CS$_2$, p-xylene, chlorobenzene, and cyclohexane can be used as a sulfur solvent solution, with CS$_2$ showing the highest sulfur solubility. Toluene has a high solubility to sulfur at a higher temperature (11.6/100 g at 80 °C), and its toxicity is much lower than CS$_2$. Thus, toluene was determined to have the potential to replace the common use of CS$_2$. On the other hand, the dissolving sulfur in the saturated toluene solution would remarkably reduce to 2.0/100 g at 25 °C. The variation solubilities with temperature make it possible to further separate sulfur from the toluene solution. After the purification process, the toluene solution can be recycled. Figure 4a shows the sulfur has been completely removed using toluene as a sulfur-dissolving agent, leaving pure-phase pyrite as the final product.

While the Fe/S ratios decided the iron sulfide phases, the reaction time significantly affects the thermal stability, particle size, and morphology of synthetic pyrite. The thermogravimetric analysis (TGA) curves in Figure 5c illustrate two stages of weight loss for 1 h, 2 h, and 4 h synthetic pyrite. According to reactions 1 and 2, in the whole heating process from 30 to 800 °C, the synthetic pyrite first decomposed to pyrrhotite (FeS$_{1-x}$, 0 < x < 0.125) and eventually troilite (FeS). The theoretical weight loss from pyrite to troilite is 26.7%, which is consistent with the weight loss of 4 h synthetic pyrite, 26.2% in Figure 5c. The weight losses of 1 h and 2 h synthetic pyrite were 25.5 and 26.2%, respectively. Increasing the reaction time marginally improved the thermal stability of synthetic pyrite.46 The decomposition process comparing to natural pyrite showed more weight loss for synthetic pyrite than for natural pyrite. This may be attributed to the much smaller specific surface area of natural pyrite due to extensive aggregation during its formation.
in the crust. The larger surface area of synthetic pyrite has more exposed nanoparticles to release gaseous sulfur during the pyrolysis.

Morphology control of pyrite synthesis is essential due to its multiple application as a functional material. Although adding surfactants (e.g., ethylene glycol, polyvinylpyrrolidone, and Triton X-100) can effectively control the morphology of the synthetic pyrite, they can introduce impurities to and alter the conductivity of the product. To better illustrate the relationship between the electrical properties and dissolution behavior for hydrothermal formed pyrite, no surfactant was used in the current study. The effect of reaction on the morphology was studied for 1, 2, and 4 h synthetic pyrite. The 1-h pyrite SEM image shows well-dispersed microspheres distributed irregularly on the mineral surface (Figure 6a,c), similar to the pyrite synthesized using ethylene glycol as a surfactant for 12 h. The monodisperse microsphere structure has been approved to have great electrochemical performance as an electrode in solar cells and anode for battery material. Thus, employing the hydrothermal method at a reaction time of 1 h or less, without surfactant, permitted control of the morphology of the pyrite products. On further increasing the reaction time, irregular morphology due to significant aggregation was observed on 4 h synthetic pyrite (Figure 6d). The significant aggregation also leads to the increasing particle size with reaction time, as shown in Figure 5b.

3.2. Electrochemical Properties of Synthetic Pyrite. The electrical properties of pyrite are essential to be investigated with regard to their functional material fabrication. However, the fact that is often neglected is that the electrical properties also relate to pyrite dissolution behavior given pyrite has long been recognized as a semiconducting mineral. The dissolution of pyrite can be treated as an electrochemical process in which electrons transfer from sulfur atoms at the anodic site to the oxidants (Fe²⁺, dissolved oxygen) on the cathodic sites. The charge transfer process is inevitably affected by the electrical properties of pyrite. Lehner et al. found that variations in conductivity could play a role in charge transfer kinetics. A recent electrochemical study of n-type pyrite oxidation suggested that the rate-limiting step is the ferrous oxidation on the pyrite surface, which links to the n-type semiconducting property. Anyhow, the definite correlations between the electrical properties of pyrite and the chemical and electrochemical reactivity of the mineral are still unclear. Here in this study, the inner link between the pyrite dissolution kinetics and its electrical properties (conductivity and semiconducting properties) were explored.

The dissolution kinetics was analyzed via the Tafel analysis method. A novel method was applied to measure the conductivity of synthetic pyrite (Figure 3). Characterizing the semiconductor properties using Mott–Schottky plots has been conducted with pyrite in sulfuric acid solution. Pyrites synthesized for 1, 2, and 4 h were used as raw materials; the results can be instructive for pyrite hydrothermal ore oxidation in nature.

Previous research demonstrated that the pyrite in nature has a wide conductivity range between 0.002 and 50 S/cm, which was presumably related to the trace element composition. Generally, the n-type pyrite has higher conductivity than p-type pyrite. The conductivity measurement results showed the pyrite samples have a relatively high conductivity range between 3 and 15 S/cm. With increasing reaction time, the conductivities of pyrite increased. The trend of conductivity change could be the strengthening of interfacial bonding after a longer reaction time. The linear sweep voltammetric (LSV) measurement was conducted on 3 pyrite samples in a 0.5 M sulfuric acid solution in a potential range from −0.1 V vs OCP to 0.1 V vs OCP. The polarization behavior and kinetics parameters after Tafel analysis are presented in Figure 9 and Table 1. The iₒ decreased with reaction time for pyrite, from 9.12 × 10⁻⁶ to 1.58 × 10⁻⁶ A/cm² for 4-h pyrite, which suggests a decreasing dissolution rate for pyrite synthesized for a longer time. The equilibrium potential (E°) increased with synthesis time (Table 1), from 0.40 V for 1-h pyrite to 0.44 V for 4-h pyrite. When oxidants such as Fe³⁺ are present in the electrolyte, the pyrite with a smaller E° tends to dissolve faster since the reaction driving force is the potential difference between the oxidant and the pyrite. The anodic charge transfer coefficient (αₐ) increased with reaction time whereas the cathodic charge transfer coefficient (αₗ) decreased (Table 1). The sums of anodic and cathodic charge transfer coefficients (n) approached 1, which suggests a single electron transfer reaction on the surface of the pyrite electrode. The much smaller anodic than cathodic transfer coefficients indicates an n-type semiconductor property. Moreover, the Mott–Schottky analysis was applied to validate the semiconductor properties for the pyrite–sulfuric acid solution interface. The Mott–Schottky plots were acquired by the eq 5.

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0N} \left( E - E_B - \frac{kT}{e} \right)$$

where ε is the dielectric constant, ε₀, the permittivity of free space, e the charge of an electron, N the donor density, E the applied potential, E_B the flat band potential, k the Boltzmann constant, and T the absolute temperature. As shown in Figure 10, the Mott–Schottky plot of synthetic pyrite samples shows typical n-type semiconductor properties, where the Mott–Schottky plot has a positive slope, until the break potential of about 0.6 V. In the first potential range (from OCP to 0.6 V), pyrite was oxidized and a passive film was formed (reaction 6).

$$\text{FeS}_2 \rightarrow \text{Fe}^{2+} + 2\text{SO}_4^{2-} + 2e^-$$

In the above equation, the SO₄ refers to a sulfur-rich layer, though the composition of the layer is still under debate. The positive slopes in the potential range and low anodic charge transfer coefficients both confirm the sulfur-rich film on pyrite has n-type semiconducting properties. At potentials greater than the break potential, into the second stage of pyrite oxidation, negative slope lines for the Mott–Schottky plot were observed due to the reaction

$$\text{SO}_4^{2-} + 4\text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + 8\text{H}^+ + 6e^-$$

The abrupt change originates from the deterioration of the passive film. The dissolution of elemental sulfur accumulates mobile holes on the pyrite surface and thus changes the semiconductor properties. It was also noticed that the slope increased with synthetic time for pyrite. According to the Mott–Schottky equation (eq 5), the higher the slope, the lower the N_d. It seems the donor density decreases with reaction time for pyrite. The higher donor density for 1-h pyrite could result in an enhanced corrosion rate and thus a higher dissolution rate.

3.3. Synthesis of Bulk Pyrite Material. From the above discussion, the morphology of pyrite is likely controlled by the reaction time-dependent aggregation behavior in 4 h. Under the
same experimental conditions (Fe/S ratio of 1:4, 180 °C), and with further extension of the reaction time to 12 and 24 h, it was observed that the pyrite sheet became thicker and coarser (Figure 11). Increasing the reaction temperature to 200 °C and for reaction times of 4, 12, and 24 h, with more aggressive aggregation, a rode shape of pyrite and lump pyrite with several cm depths were formed at 12 and 24 h, respectively (Figure 11). Exploration of the bulk formation process can be significant for further research on the hydrothermal formation of pyrite in nature. Besides, bulk pyrite as a working electrode is ideal for pyrite electrochemical study. Pure-phase pyrite is desired when studying the mechanism of pyrite dissolution via electrochemical methods, considering the impurities in pyrite, such as As, Co, and Ni, can largely alter its electrical and electrochemical properties. Previous research used the pyrite-carbon paste electrode (PCPE) or slurry coating method to fabricate the pyrite working electrode. However, these techniques exhibit several disadvantages, like weaker fabrication reproducibility and mechanical stability compared with the bare solid electrodes. This bulk mineral, which has not been shown in previous research, is of particular interest in metallurgy and environmental engineering and will be the subject of related work in the future.

4. CONCLUSIONS

This paper describes a cost-effective, easy-to-operate, low-temperature, and nontoxic hydrothermal method to synthesize pyrite. After purification using a hot toluene solution to dissolve sulfur, phase-pure pyrite can be produced. At a Fe/S molar ratio of 1:4, the synthetic FeS₂ phase contains pyrite only: no marcasite was found. The synthetic pyrite at 180 °C exhibits a sheet shape, and the layer becomes thicker with increasing reaction time from 1 to 4 h. With increasing reaction time, the conductivity of the pyrite increased and the electrochemical activity decreased, likely due to drastic aggregation and enlargement of particle size with longer reaction times. Increasing the reaction temperature to 200 °C and reaction time to 24 h yielded bulk pyrite. This study provides a simple process to produce not only pyrite nanoparticles with a spherical shape without the use of surfactants but also bulk pyrite, which can be used to study the leaching or electrochemical behavior of phase-pure synthetic pyrite similar to pyrite mineral in nature.

5. MATERIALS AND METHODS

5.1. Pyrite Synthesis. The reagents used for pyrite synthesis were iron sulfate heptahydrate (FeSO₄·7H₂O, Anachemica), sodium thiosulfate pentahydrate (Na₂S₂O₅·5H₂O, Fisher Scientific), and deionized (DI) water. The main reactor was a 2 L stainless steel autoclave (4572 Pressure Reaction system, Parr Instrument Company) equipped with a temperature and mixing controller. To avoid corrosion from the reaction, a customized glass liner was installed within the reactor.

To synthesize pyrite particles, the molar ratios of Fe/S sources were 1:1, 1:2, and 1:4, respectively. Iron sulfate heptahydrate
(0.16 mol, 44.48 g) and sodium thiosulfate pentahydrate (0.16, 0.32, and 0.64 mol or 39.71, 79.42, and 158.84 g) were dissolved in 800 mL of DI water and transferred to the reactor (Figure 11). The solution pH without adjustment was determined to be 4.5. Synthesis reactions were run at 180 °C, 400 rpm mixing rate, and 1, 2, and 4 h reaction times to investigate the formation mechanism of pyrite. Bulk pyrite synthesis was attempted at 180 and 200 °C for 4, 12, and 24 h. After the reaction was complete, the pH of the solutions decreased to approximately 0.4. The solid products were cooled to room temperature, filtered with DI water several times, and dried at 40 °C in an oven.

Because the hydrothermal reaction produces macroscopic elemental sulfur, a purification step is required. The dry products were subjected to grinding in an agate mortar and transferred to a beaker containing 100 mL of toluene (Figure 11). The toluene solution was heated to near boiling (110 °C) for 2 min; then, vacuum filtration (particle retention: >11 μm) was used to separate the sulfur-rich solution and sulfur-free solid product (pure pyrite). The synthetic pyrite was washed three times with reagent-grade ethanol and DI water and dried in a vacuum oven at 40 °C for 6 h. The toluene solution was cooled to room temperature to permit spontaneous precipitation of elemental sulfur, followed by vacuum filtration (particle retention: >11 μm) to obtain pure elemental sulfur. The toluene solution could then be reused.

5.2. Characterization. The solid products before and after the purification process were characterized by X-ray powder diffraction (XRD) using an XPert Pro Philips powder diffractometer. X-ray photoelectron spectroscopy (XPS; VG ESCALAB-3MKll XPS) was also conducted to study the Fe, S, and O species in the products. The XPS instrument was equipped with an Al Kz source, 300 W (15 kV, 20 mA), and the binding energy calibration was based on C 1s at 284.4 eV.

The morphology (cross-sectional and whole-particle) of the synthetic pyrite was analyzed with an FEI NovaSEM scanning electron microscope (SEM). To obtain a cross-sectional view, samples were embedded in epoxy resin and ground using 1200-grit silicon carbide paper to expose the cross sections and polished by 1 μm diamond paste. An aberration-corrected FEI Titan scanning transmission electron microscope (TEM), operating at an accelerating voltage of 200 kV in TEM mode, was used to produce high-resolution TEM images to investigate the microstructure and measure the particle size of the products. To investigate the thermal stability of synthetic pyrite, thermogravimetric analysis (TGA) was carried out in closed alumina crucibles on a Netzsch STA449 F3 Jupiter apparatus at a heating rate of 5 K/min and a N2 flow rate of 40 mL/min. The rough particle size of the samples was analyzed by a laser particle size analyzer.

5.3. Electrochemical Measurements. The conductivity of the synthetic pyrite was investigated using equipment designed to measure the conductivity of iridium catalyst powder. The pyrite powder (approximately 0.1 g) is compressed with N2 gas between a pair of brass pistons located in an acrylic cylinder to create constant electrical contact between minerals (Figure 12); then, the resistivity can be directly measured by a multimeter. Initially, the resistivity is related to the applied pressure, until it reaches a stable value when the powder is highly compact. The compressed pyrite powder had 3 mm diameter and the height of the compressed pyrite powder was recorded. The powder conductivity or resistivity was calculated by

\[ \sigma = \frac{1}{\rho} = \frac{l}{R_p \times \left( \frac{1}{A} \right)} \]

where \( \sigma \) is the conductivity (Siemens/cm), \( \rho \) is the resistivity (Ω cm), \( R_p \) is the electrical resistance (Ω) of the compressed powder obtained from the multimeter, \( l \) is the height of the compressed powder minerals, and \( A \) is the surface area (cm²) of the compressed mineral column.

Pyrite oxidation behavior relative to synthesis time was studied by a series of electrochemical tests on a fabricated (see ref 63 for details) pyrite-carbon paste electrode (PCPE). This working electrode had an active area of 0.2 cm². A graphite rod was the counter electrode, and an Ag/AgCl electrode with a 3 M KCl internal solution acted as a reference electrode. All potentials in this paper are vs the Ag/AgCl reference electrode. Before each test, the working electrode was loaded with fresh paste, polished, and then immersed in the electrolyte, a 0.5 M sulfuric acid solution. The electrochemical experiment only began when the working electrode reached a stable open circuit potential (OCP) in the electrolyte. The polarization potential was measured on a GSTAT302N potentiostat (Metrohm) from 0.3 to 0.9 V and a frequency of 1 kHz. The electrochemical results were analyzed by Nova software (Version 2.3).

Tafel analysis by linear sweep voltammetry (LSV) was implemented to determine the PCPE oxidation rates. LSV tests were conducted in the potential range from −0.1 V vs OCP to +0.1 V vs OCP at a 1 mV/s scan rate. Important kinetic constants were calculated according to Tafel equation and anodic and cathodic Tafel equations, respectively, as follows:

\[ i = i_0 e^{-\eta F} \]

\[ \log(i_A) = \log(i_0) + \frac{\alpha nF\eta}{2.3RT} \]

\[ \log(i_C) = \log(i_0) - \frac{\alpha nF\eta}{2.3RT} \]

such as \( i_0 \) (exchange current density), \( E_0 \) (equilibrium potential), anodic transfer coefficient (\( \alpha_a \)), and cathodic transfer coefficient (\( \alpha_c \)). For other parameters, \( \alpha \) is the transfer coefficient, \( f = F/RT \), \( \eta \) is the overpotential (\( E - E_{eq} \)), \( i_A \) is the anodic current density, and \( i_C \) is the cathodic current density.

Mott–Schottky tests were run to evaluate the semiconductor properties of the synthetic pyrite. The Mott–Schottky plots show the relationship between the applied potential and
measured capacitance on the electrode—electrolyte interface.\textsuperscript{64} The frequency was set at 1 kHz, and the potential range was chosen between 0.3 and 0.9 V.

\section*{AUTHOR INFORMATION}

Corresponding Authors

Lin Li – The Robert M. Buchanan Department of Mining Engineering, Queen’s University, Kingston, Ontario, Canada K7L 3N6; \textsuperscript{1} orcid.org/0000-0002-9109-6233; Email: lin.li@queensu.ca

Ahmad Gahreman – The Robert M. Buchanan Department of Mining Engineering, Queen’s University, Kingston, Ontario, Canada K7L 3N6; \textsuperscript{1} orcid.org/0000-0002-3568-7880; Email: ahmad.g@queensu.ca

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c03613

Notes

The authors declare no competing financial interest.

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