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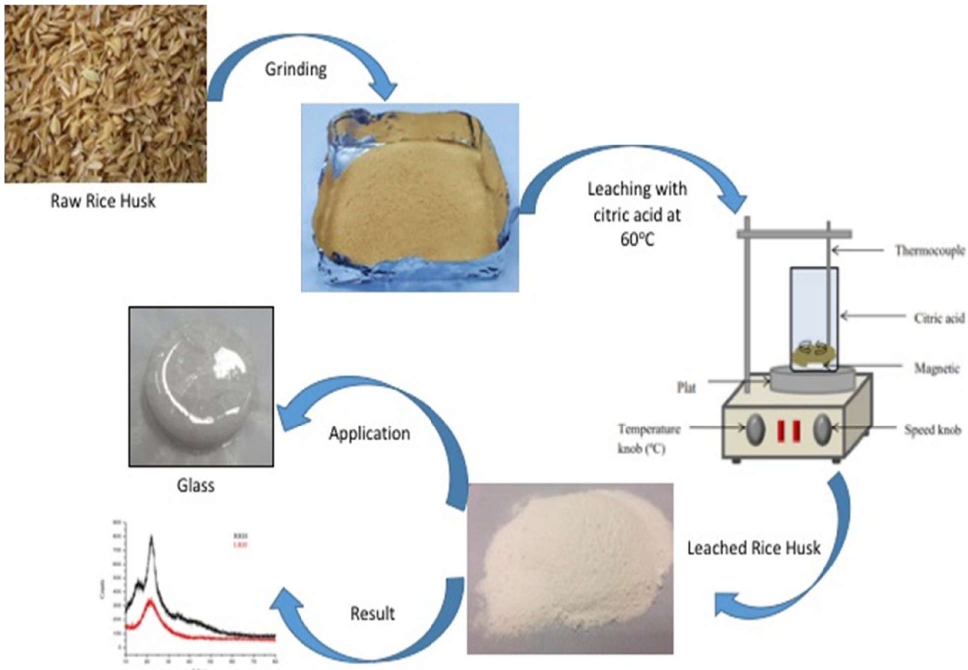
AMORPHOUS MICROSTRUCTURAL EVOLUTION AND IMPURITY REMOVAL IN ACID-LEACHED RICE HUSK

This study investigates the microstructural transformations of rice husk, with a focus on the amorphous-to-crystalline phase transition and the impact of acid leaching treatments. Recognizing rice husk's potential as a source for high-purity silica materials, the research explores the influence of treatment sequences and citric acid concentrations on microstructure and impurity removal. Utilizing X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM), the study analyzes leached rice husk samples subjected to varied acid leaching conditions. Notably, XRD reveals a consistent amorphous phase in both leached rice husk (LRH) and leached rice husk ash (LRHA), independent of pre-treatment methods. SEM images demonstrate enhanced SiO_2 particle morphology at different citric acid concentrations compared to raw rice husk particles. The nuanced interplay between treatment sequences, acid concentrations, and resulting microstructures is highlighted, indicating the potential for tailored high-purity silica materials from rice husk. The presence of pores in rice husk ash further underscores the efficacy of acid leaching in impurity removal. In conclusion, the study offers a comprehensive understanding of amorphous microstructural evolution in rice husks, presenting opportunities for controlled microstructure development in the production of high-purity silica materials.

Keyword: Amorphous; leaching; rice husk; silica

Graphical Abstract:



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1. Introduction

Rice, one of the world's staple crops, yields over 650 million tons annually, producing approximately 220 kg of rice husk per ton of paddy rice. This byproduct, known as rice husk (RH), has gained attention as a valuable renewable resource for energy production and high-purity silica (SiO_2) extraction [1]. The abundance of rice husks presents economic opportunities for industrial applications. Additionally, enhancing the crystallinity and purity of rice husk through acid leaching treatment is a crucial aspect for achieving improved thermal stability [2-5].

Despite its potential, a significant challenge arises from the presence of metallic impurities in rice husk, which can adversely impact the quality of derived products [6,7]. This issue becomes particularly crucial in applications such as the manufacturing of colorless glass, optical fibers, and high-purity ceramics [8]. The iron content (Fe_2O_3) in quartz sand, influenced by the usage of rice husk, dictates the suitability of floated material for glass production [9].

The primary objective of this study is to develop optimization methods for the reduction of impurities in rice husk, thereby enhancing the production of high-purity silica with improved thermal stability. This involves a meticulous control of parameters during acid leaching treatment, including the molarity of a citric acid solution, operating temperatures, and operating times. By achieving this, the research aims not only to upgrade silica production but also to address environmental concerns related to the pollution caused by burning husks and their ashes in agricultural fields.

2. Materials and methods

The primary raw material for this study is rice husk, sourced from the northern region of Peninsular Malaysia. The chemical composition of the raw rice husk used has a low purity of silica (SiO_2) content of 77.10% as shown in TABLE 1.

To ensure the purity of the material, the rice husk underwent a meticulous cleaning process. Distilled water was employed to thoroughly wash away any soil and dust adhered to the husk, preventing any potential interference with the subsequent processes. Subsequently, the cleaned rice husk was left to dry overnight in an oven. There are four distinct states of conditions were investigated in this study:

i. Raw Rice Husk (RRH): Untreated and in its natural state.
ii. Rice Husk Ash (RHA): Obtained through controlled burning of rice husk.
iii. Leached Rice Husk (LRH): Subjected to specific treatment processes.
iv. Leached Rice Husk Ash (LRHA): A combination of treatment and controlled burning.

For the preparation of citric acid solutions, citric acid powders (SIGMA-Aldrich, purity; ≥99.5%) were dissolved in distilled water at ambient temperature. The process involved placing 20 g of rice husks into a 500 ml citric acid solution in a Griffin beaker. Operational parameters such as citric acid concentration, solution temperature, and stirring time were carefully controlled. The concentration and solution temperature were set at 1.0 M and 70°C, respectively. Stirring was performed at a constant speed of 600 rpm for 12 hours using a thermostat magnetic stirrer hotplate 85-2.

After the acid leaching process, water rinsing treatment was executed at room temperature using distilled water to eliminate any residual citric acid content from the husks. The substrate obtained from the filtration of washed rice husk was then dried overnight in the oven.

The content of silica (SiO_2) and other metallic oxides in the prepared samples was measured using XRF [10]. The analysis was conducted with a PAN analytical Model Minipal 4 PW4030. The prepared samples underwent XRD analysis, scanning from 2θ; 10°-80° at a rate of 1°/s. The X-ray Diffractometer used was a Shidmazu XRD-6000, with Cu Kα radiation (λ = 0.154 nm) generated at 30 kV and 10 mA [11]. The morphological study of each sample was observed using a JEOL JSM-6460LA SEM [12].

3. Results

3.1. Effect of acid leaching on chemical composition

LRH underwent leaching using a 0.1M citric acid solution, with the leaching treatment temperature controlled at 70°C for 1 hour, followed by combustion. The results reveal a remarkable transformation in the chemical compositions, particularly in silica content, and the reduction of impurities such as K_2O, CaO, and Fe_2O_3. The silica content in LRH exhibited a substantial increase, rising by 22.43 wt.% from 77.10 wt.% to 99.53 wt.% as shown in TABLE 2. This noteworthy enhancement underscores the effectiveness of the acid-leaching treatment in enriching silica content [13]. Specifically, the iron content in LRH decreased from 0.16 wt.% to 0.71 wt.%, indicating a significant reduction in impurity content through acid-leaching treatment.

During this process, organic constituents (cellulose, hemicellulose, and lignin) and unwanted inorganic metallic ions were separated as a liquid from the citric acid-leached suspension [14]. Solid ingredients, particularly silica particles, were obtained through filtration onto the leached rice husk. The decreased impurity levels are attributed to chemical reactions between

TABLE 1

Chemical compositions of raw rice husk

Composition	SiO_2	K_2O	CaO	CuO	Fe_2O_3	ZnO	PdO	MnO	Others
Weight	77.10	15.40	3.27	0.49	0.87	0.08	1.40	0.66	0.40

TABLE 2

Comparison of Chemical composition between RRH and LRH

Concentrations (wt.%)	RRH	LRH
SiO_2	77.10	99.53
K_2O	15.4	—
CaO	3.27	—
CuO	0.49	0.03
Fe_2O_3	0.87	0.16
ZnO	0.08	—
PdO	1.4	—
MnO	0.66	0.02
Others	0.4	0.26

the acid and metals, followed by the removal of metals through filtration [15].

To further enhance the purity of silica particles, repetitive water rinsing treatments were conducted on the acid-leached rice husks. This meticulous washing process effectively removed residual acid solution from the rice husks, ensuring the purity of the obtained silica particles. The combined approach of initial acid washing and subsequent water rinsing not only facilitates the removal of impurities but also contributes to the overall enhancement of silica purity in the leached rice husk [16].

3.2. Effect of acid leaching treatment on the amorphous phase of rice husk

The diffractogram presented in Fig.e 1 illustrates the phase characteristics of rice husk both before and after acid leaching treatment, revealing a consistent amorphous phase in both instances. Importantly, this observation underscores that the transformation from amorphous to crystalline is independent of the employed pre-treatment method [17-19].

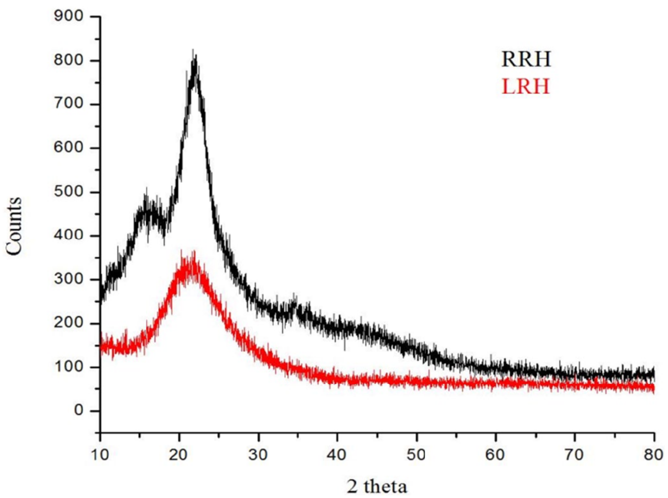

Fig. 1. Amorphous phase of raw rice husk (RRH) and leached rice husk (LRH)

When rice husk is subjected to acid leaching, it typically reacts with the mineral components in the rice husk, particularly silica (SiO_2), which is a major component contributing to the crystalline structure. The reaction between the acid and silica can lead to the removal of crystalline structures, leaving behind a more disordered, amorphous matrix. The acid breaks down the bonds in the crystalline structure, causing the material to lose its ordered arrangement and become less defined in terms of its microstructure.

Given that the silica in rice husks exists in an amorphous phase [20], the citric acid leaching treatment emerges as a favorable method for producing high-purity amorphous silica. This amorphous silica, with its distinctive properties, becomes an ideal precursor for the production of clear glass. The choice of maintaining the amorphous form is critical, as the inherent properties of glass are amorphous.

The amorphous nature of the silica obtained through citric acid leaching treatment aligns seamlessly with the requirements for clear glass production. This process ensures that the final product possesses the desired properties conducive to the production of high-quality, transparent glass.

In conclusion, the XRD results affirm the persistent amorphous phase in rice husk, emphasizing the independence of the phase transformation from the pre-treatment method [21,22]. The strategic use of citric acid leaching treatment further enhances the potential for producing high-purity amorphous silica, contributing significantly to the clear glass manufacturing process.

3.3. Effect of various acid concentrations on the amorphous phase of LRH

The diffractograms presented in Fig. 2 depict the phase characteristics of Leached Rice Husk (LRH) subjected to diverse citric acid solution concentrations at 40°C for 1 hour. A comprehensive analysis of the diffractograms, as outlined in the accompanying table, reveals a consistent amorphous structure across all samples at different citric acid concentrations.

Particularly, all LRH samples exhibit a uniform amorphous structure exclusively composed of silica. The absence of any discernible crystalline peaks in the XRD pattern signifies the complete suppression of crystallization, reaffirming the predominant amorphous nature of the samples. The XRD patterns further corroborate the amorphous nature, as evidenced by the absence of sharp peaks. Instead, a distinctive broad and intense peak at $2\theta = 20°$ dominates the spectrum, representing the silica particles within the samples [21,22].

These findings provide valuable insights into the impact of varying citric acid concentrations on the phase composition of LRH. The consistent amorphous structure, irrespective of concentration, suggests the robustness of the amorphization process under the specified conditions. The presence of a broad intense peak at $2\theta = 20°$ serves as a characteristic indicator of silica particles [21,22]. This specific peak, observed across all samples, underscores the homogeneity in the amorphous silica structure obtained through citric acid leaching at 40°C for 1 hour.

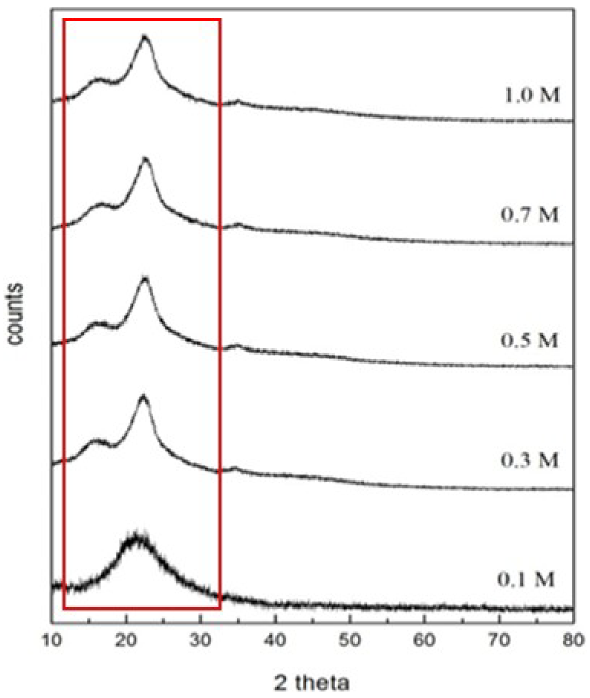

Fig. 2. Amorphous phase of leached rice husk (LRH) at various concentrations of citric acid

In conclusion, the comprehensive diffractogram analysis establishes the uniform amorphous nature of LRH samples under varied citric acid concentrations. The absence of crystalline peaks and the distinctive $2\theta = 20°$ peak highlight the effectiveness of the citric acid leaching process in maintaining a consistently amorphous structure, offering significant implications for material applications and further research endeavors.

The X-ray diffraction (XRD) patterns for both Leached Rice Husk (LRH) subjected to leaching followed by combustion and LRHA undergoing combustion followed by leaching are illustrated in Fig. 3.

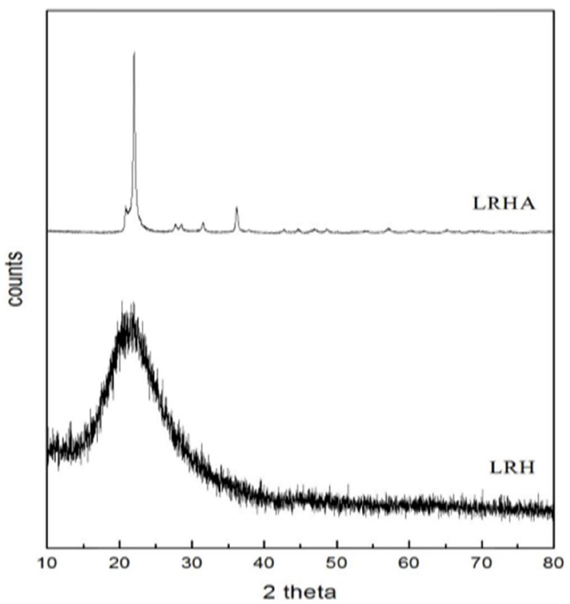

Fig. 3. X-ray diffraction pattern of leached rice husk ash (LRHA) and leached rice husk (LRH)

The shift from amorphous (LRH) to crystalline (LRHA) reveals that reversing the purification treatment sequence initiating with combustion followed by acid leaching is not preferable for attaining high-purity silica [23]. This observation underscores the critical role of treatment sequence in determining the phase of the resulting silica.

The structure of silica in rice husk ash strongly depends on the combustion of the rice husk. It indicates that the changes from originally amorphous structures to crystal ones occur by combusting the rice husk at 1050°C or more.

3.4. Effect of acid concentration on morphology of RHA

Fig. 4 displays microstructure images magnified at 5000×, illustrating the microstructural evolution of SiO_2 particles under different citric acid concentrations at 40°C for 1 hour. SiO_2 particles leached at 0.1 M exhibit agglomeration, with irregular shapes and non-uniform surface distribution. This agglomerated irregularity persists across concentrations from 0.3 M to 1.0 M.

The observed SiO_2 particles present superior characteristics compared to the raw rice husk cluster-type particles. Nanoparticles exhibit a mixture of uniform and agglomerated species with varying sizes. Acid leaching of rice husks induces fragmentation of rice husk ash particles, introducing a few pores. The silica in rice husk ash reacts with citric acid, prompting a chelate reaction that effectively removes impurities, resulting in the detection of pores between silica particles.

To exert control over the microstructure of silica particles from rice husk ash, a combination of acid and/or alkali leaching (e.g., HCL, HNO_3, H_2SO_4, and NaOH) along with combustion of rice husk within the temperature range of 500-1100°C proves effective.

3.5. Effect of combustion on purification of silica

The colour of rice husk ash generally indicated the completeness of the combustion process and the structural phase of the ash. Figs. 5(a) and 5(b) display images of rice husk ash that had completely changed from black to white. RHA, which is the product of rice husk without acid leaching treatment, appeared overall greyish, with no traces of white ash due to unburnt carbon remaining within the rice husk. When the rice husk was not treated, the impurity oxides enhanced the surface melting of silica, trapping carbon within the silica. As more residual carbon became entrapped, the colour of the rice husk darkened. The colour of rice husk ash varied from black to white depending on the amount of unburnt and inorganic carbon present.

To understand the effect of chemical treatment on the whiteness of silica, rice husk was leached at different concentrations of citric acid solution. The images of rice husk ash showed a visibly white colour with no traces of black carbon particles. The complete white colour of the rice husk ash indicated the

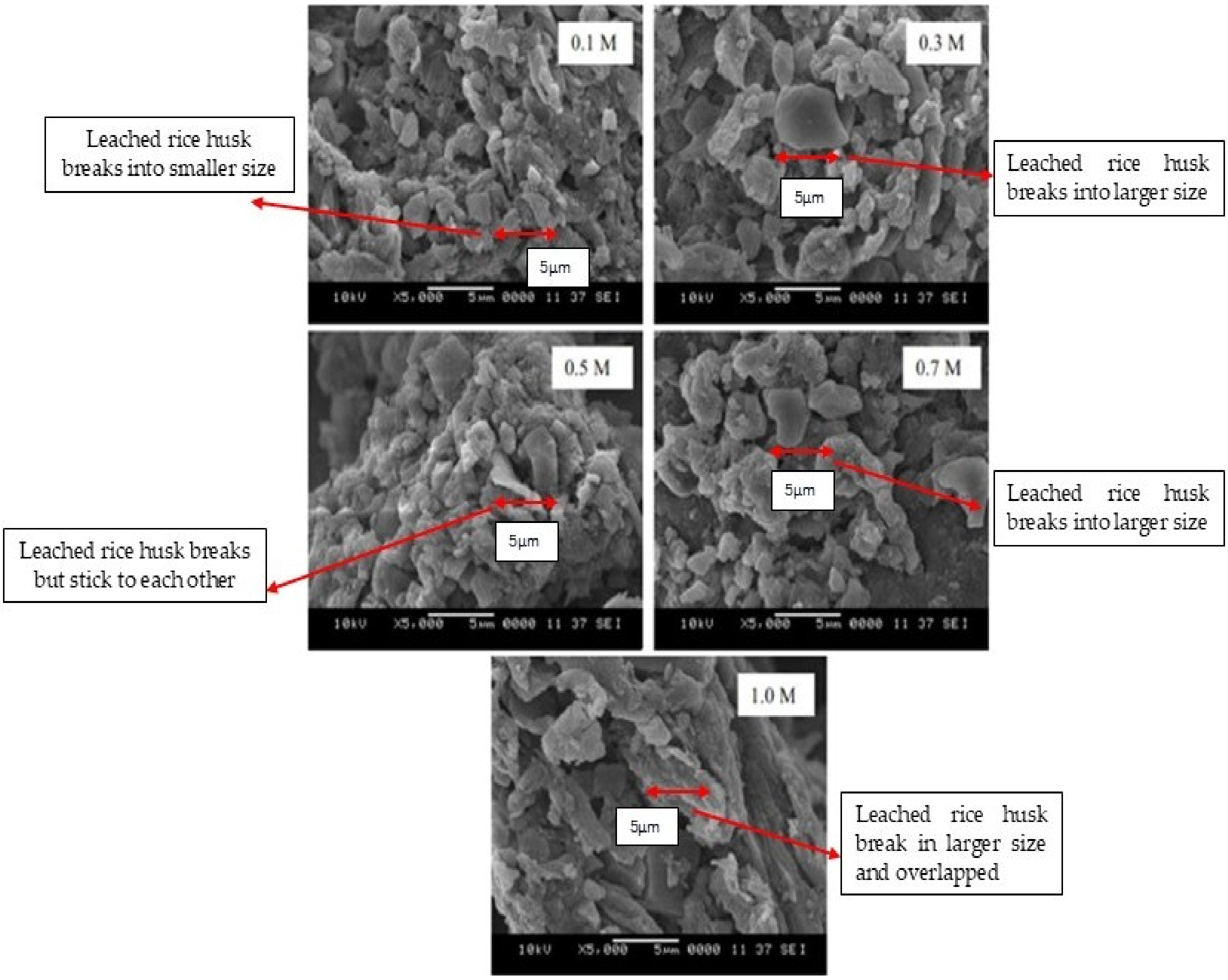

Fig. 4. Microstructure images of magnified leached rice husk at various concentrations of citric acid

presence of amorphous high-purity silica. Thus, the pre-treatment process of removing metal oxides, especially K_2O, increased the brightness and whiteness of the silica.

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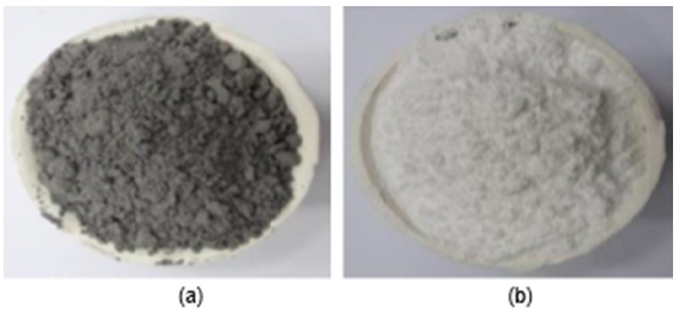

Fig. 5. (a) Greyish rice husk ash (b) White rice husk ash

White ash indicated the complete oxidation of carbon, which also signified a large proportion of amorphous silica in the ash. At high temperatures, a strong interaction between potassium and silica ions caused the formation of potassium polyciliate combined with carbon, resulting in grey-coloured ash. When the husk was pretreated with acid, a significant portion of its potassium was removed, preventing the ash from attaining a grey colour.

4. Conclusions

In conclusion, the comprehensive investigation into the microstructure of rice husk, particularly the transition from an amorphous to the crystalline phase, has provided valuable insights into the pivotal role of acid-leaching treatments. The XRD results highlighted a consistent amorphous phase in both leached rice husk (LRH) and leached rice husk ash (LRHA), underscoring the independence of this phase transformation from the pre-treatment method. The SEM images further elucidated the impact of citric acid concentration on the microstructure of SiO_2 particles, with a noticeable improvement over raw rice husk particles and distinctive variations in morphology at different concentrations. Importantly, acid leaching was observed to induce the fragmentation of rice husk ash particles, creating pores and facilitating the removal of impurities through chelate reactions with citric acid. Citric acid has proven to be an effective leaching agent in the acid leaching treatment, yielding satisfactory results in removing impurities from rice husks. Citric acid was chosen due to its environmentally friendly and economical properties. The ability to control the microstructure of silica particles from rice husk ash through acid and/or alkali leaching, coupled with combustion, opens promising avenues for tailoring high-purity silica materials with diverse applications. Hence, the purity of silica achieved exceeded 99% with minimal impurity content. The optimal conditions for this purity were a 0.1 M citric acid solution at a temperature of 40°C with a stirring time of 1 hour. Metallic impurities were effectively removed during the acid leaching treatment.

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