A mild route for the preparation of calcium carbonate rod bundles in large scale from carbide slag

1 | INTRODUCTION

Industrial solid waste has cascaded detriments on the environment and further sustainable development of mankind, due to the high output and the difficulty of treatment. Carbide slag, as one of the industrial solid wastes on a large scale, is the by-product of the production of acetylene using calcium carbide. As the main component of carbide slag is Ca(OH)₂, thus its comprehensive utilization to prepare value-added products, such as CaCO₃, has high economic value and environmental protection effects [1–3]. CaCO₃ is an industrial filler with excellent performance and low price, which has been widely used in rubber, plastics, coatings, paper, ink, and other industries. CaCO₃ has various crystal forms, including calcite, aragonite, and vaterite. As to the aragonite, it is unstable and easy to turn into calcite in nature [4], which belongs to the orthorhombic system and mainly performs as columnar or fibrous morphology, and occasionally dendritic morphology [5].

In recent years, inspired by the biomineralisation process, researches on “controllable synthesis” of CaCO₃ have received much more attention. Crystal modifiers, such as organic additives and surfactants, are generally added in the nucleation and growth process to control the morphology and structure of CaCO₃ [6–9]. Zheng et al. [10] used the CaCl₂ and Na₂CO₃ as raw materials to synthesize CaCO₃ hollow microspheres with calcite and vaterite composite crystal forms by adding polyacrylic acid (PAA) and sodium dodecyl sulphate (SDS) as the crystal control agents. Zhao et al. [11] prepared the conch-like CaCO₃ particles from CaCl₂ via a liquid-phase precipitation method to using Bi(NO₃)₃ as an additive. However, the synthesis of CaCO₃ with highly regioselective kind of crystalline structure, especially the aragonite, still suffers from lacking strategies.

Herein, we described a straightforward way to prepare uniform CaCO₃ rod bundles mostly composed of aragonite from carbide slag. The CaCl₂ leaching solution was obtained by the chemical reaction between calcium carbide slag and ammonium chloride. Afterward, the CaCl₂ was carbonized with Na₂CO₃ to synthesize aragonite CaCO₃ rod bundles in the existence of crystal modifier (ethylene glycol), thus realizing a controllable synthesis of CaCO₃ with uniform morphology and particularly crystalline structure under mild conditions.

2 | EXPERIMENTAL SECTION

Ammonium chloride (NH₄Cl, Sinopharm Chemical Reagent Co., Ltd., ≥99%), sodium carbonate (Na₂CO₃, Sinopharm Chemical Reagent Co., Ltd., ≥99%), ethylene glycol ((CH₂OH)₂, Sinopharm Chemical Reagent Co., Ltd., ≥99%) were used without any further purification. The carbide slag was provided by CNSG Anhui Hong Sifang Co., Ltd.

Figure 1 shows the process flow chart for the preparation of calcium carbonate from carbide slag. In a typical process, 417.5 g of NH₄Cl and 338 g of carbide slag were thoroughly mixed in 2000 mL of deionized water via vigorous stir and reacted for 1 h under ambient temperature. The resultant mixture was filtered to obtain a transparent solution containing about 1.5 mol L⁻¹ Ca²⁺. Afterward, 240 mL of 0.5 mol L⁻¹ Na₂CO₃ solution was dropped into the solution consists of 100 mL of the as-obtained Ca²⁺ solution, 200 mL of deionized water, and 0–40 mL of (CH₂OH)₂ while stirring (300 rpm) at a constant temperature. After stirring for another 30 min, the precipitate was filtered and washed with deionized water and ethanol, and adequately dried in an oven at 70 °C. The resulting white powders were the calcium carbonate.

The concentration of Ca²⁺ in the solution was determined by EDTA complexometric titration. The phase and structure of CaCO₃ samples were characterized by X-ray diffraction (XRD, D/max-γB diffractometer, from Japan science corporation), CuKα ray with the tube voltage of 40 kV and current of 100 mA, scanning speed: 4°·min⁻¹ and range: 2θ from 5° to 70°). The morphology of the CaCO₃ sample was observed by field emission scanning electron microscope (FESEM, SU8020 electron microscope, from Hitachi, the samples were ultrasonically dispersed for 10 min with ethanol, dropped on the cleaned silicon wafer, then tested with accelerating voltage 15 kV after the surface was sprayed with gold). The microstructure of the sample was observed by a high-resolution electron transmission electron microscope (HRTEM, JEOL-2010 transmission electron microscope, from Nippon electronics, acceleration voltage: 100 kV, dot and stripe resolution: 0.194 and 0.14 nm, respectively). The characteristic groups of the samples were characterized by Fourier transform infrared spectroscopy (FT-IR, Nicolet 67 infrared spectrometer, from Thermo Nicolet, mid-infrared-ATR attenuated total reflection method, scanning wavelength range: 500–4000 cm⁻¹).
3 RESULTS AND DISCUSSION

Figure 2 shows the FESEM images of the CaCO₃ samples prepared with different addition volumes of ethylene glycol (the concentration of Ca²⁺: 0.5 mol·L⁻¹, the reaction temperature: 80 °C, and the reaction time: 30 min).

The FESEM images in Figure 2 depict that the CaCO₃ sample is regularly granulated without the addition of ethylene glycol (Figure 2(a)). The CaCO₃ sample appears as uniform rod bundles with the addition of 30 mL ethylene glycol (Figure 2(b)). Each bundle is grown from a plurality of rod-shaped CaCO₃ branches of about 2 μm in length and about 200 nm in diameter, indicating that the addition of ethylene glycol plays a crucial role in modulating the nucleation and growth of CaCO₃.

Figure 3 shows the XRD pattern of the CaCO₃ rod bundles sample. It can be seen from the pattern that the CaCO₃ sample is mainly composed of aragonite(a) (PDF 71–2396) and calcite(c) (PDF 85–1108). According to the literature [12], the content of aragonite in the mixed phases can be calculated as follows:

\[
y = \left(1 - \frac{1}{1 + 3.9I_A/I_C}\right) \times 100\% \tag{1}
\]

where \(y\) is the mass fraction of aragonite (%); \(I_A\) is the strongest diffraction peak (26.27°) intensity of the aragonite, and \(I_C\) is the strongest diffraction peak (29.48°) intensity of the calcite. According to the Equation (1) and the XRD pattern of the CaCO₃ sample, the mass fraction of aragonite is calculated to 94.92%. As listed in Table 1, our synthetic approach could give the highest mass fraction of aragonite among all the reported synthetic approaches till now, indicating the significant advantages of our strategy in the synthesis of CaCO₃ with highly regioselective kind of crystalline structure (the aragonite here).
TABLE 1  Summary of reported mass fraction of aragonite in the CaCO₃ samples

| Serial number | Reaction temperatures / °C | Mass fraction of aragonite / % | Refs. |
|---------------|----------------------------|-------------------------------|-------|
| 1             | 80                        | 94.9                          | This work |
| 2             | 100                       | 93.7                          | [13]  |
| 3             | 20                        | 82.0                          | [14]  |
| 4             | 40                        | 80.0                          | [15]  |
| 5             | 80                        | 70.6                          | [16]  |

Figure 4 show the high-resolution transmission electron microscope (HRTEM) image and selected area electron diffraction (SAED) diagram of the rod-shaped CaCO₃ sample. The clear diffraction spots (Figure 4(b)) and lattice fringes (Figure 4(c)) show that the as-prepared CaCO₃ sample is a single-crystalline crystal. The lattice fringe spacing is measured as 0.248 nm, which attributes to the (102) plane of aragonite CaCO₃. It is shown that the rod bundles prepared under the experimental conditions preferentially grow along the normal direction of the aragonite CaCO₃ crystal plane (102), which is consistent with the indexing results of the diffraction spots in the SAED diagram.

Figure 5 is the FT-IR spectra of CaCO₃ samples prepared with and without the addition of 30 mL ethylene glycol. The absorption peaks at 1438, 1089, 854, and 713 cm⁻¹ in the spectra corresponding to the antisymmetric and symmetric stretching vibration peak, the out-of-plane, and the in-plane bending vibration peak of CO₃²⁻, respectively. Moreover, it is found that the FT-IR spectra of the CaCO₃ samples show no characteristic absorption peak for ethylene glycol. The reason might be that ethylene glycol participates in the nucleation and growth process of CaCO₃ and plays a crucial role in regulating the formation of CaCO₃ rod bundles as demonstrated in Figure 2, however, it may be dissolved in water or ethanol and enter the liquid during the washing process due to its high solubility in water and ethanol.

![FIGURE 4 TEM and SAED images of CaCO₃ rod bundles sample. (a) TEM; (b) SAED; (c) HRTEM](image)
FIGURE 6  XRD patterns of CaCO₃ samples prepared with different addition volumes of ethylene glycol

When the initial concentration of Ca²⁺ was 0.5 mol·L⁻¹, the reaction temperature was 80 °C, and the reaction time was 30 min, the crystalline structure, and morphologies of the CaCO₃ samples prepared with additions of 10, 20, 30, 40, and 50 mL of the ethylene glycol were investigated by XRD and FESEM. The experimental results are shown in Figures 6, 7, and Table 2.

It can be seen from Figure 6 that the CaCO₃ samples prepared with different addition volumes of ethylene glycol are all mixed phases of calcite and aragonite. The mass fraction of aragonite in the sample (Table 2) increases first and then decreases with the increase of the addition of ethylene glycol. When the addition of ethylene glycol is 30 mL, the mass fraction of aragonite reaches the maximum value (94.92%).

Figure 7 shows the FESEM images of CaCO₃ samples prepared with different addition volumes of ethylene glycol. It can be seen from the images that the addition volume of ethylene glycol has a great influence on the morphology of the prepared CaCO₃ sample. When the addition volume of ethylene glycol is less or more than 30 mL (Figure 7(a,b,d)), the CaCO₃ sample shows massive or irregular rod-like morphology. When the addition volume of ethylene glycol is 30 mL, the as-prepared CaCO₃ sample performs as regular rod bundles (Figure 7(c)).

When the initial concentration of Ca²⁺ was 0.5 mol·L⁻¹, the reaction time was 30 min, and the addition volume of ethylene glycol was 30 mL, the crystalline structure, and morphologies of the prepared samples under different reaction temperatures range from 50 to 90 °C were investigated. The corresponding experimental results are shown in Figures 8, 9, and Table 3.

It can be seen from Figure 8 that the CaCO₃ samples prepared at different temperatures are all mixed phases of calcite

![Figure 7](image-url)
and aragonite. The data in Table 3 shows that the mass fraction of aragonite increases with the increase of reaction temperature. Figure 9 shows the FESEM images of CaCO₃ samples prepared at different temperatures. It can be seen from the images that the CaCO₃ samples mainly perform as squares or irregular bundles (Figure 9(a, b)) when the reaction temperature is 50 or 60 °C. The CaCO₃ sample becomes irregular bundles mixed with rods and block-like structure when the reaction temperature increases to 70 °C. When the reaction temperature is 80 °C, the as-prepared CaCO₃ sample performs as regular rod bundles in morphology and exhibits good dispersity (Figure 9(d)). Further increasing the reaction temperature as 90 °C, the CaCO₃ sample could keep the regular appearance (Figure 9(c)). As shown in Table 3, the mass fraction of aragonite in the CaCO₃ sample is generally increased by elevating the synthetic temperature, but cannot be higher than 95% after increasing the temperature over 80 °C. We herein choose 80 °C as the opportune synthetic temperature to achieve the high mass fraction of aragonite CaCO₃ in our system.

Combining the above results (Figures 7 and 9, and Tables 2 and 3), it can be clearly seen that the regularity of the CaCO₃ rod bundles is positively correlated with the mass fraction of aragonite. When the mass fraction of aragonite is low, the sample mainly performs as block or irregular rod shape. When the mass fraction of aragonite is high, the sample mainly performs as relatively regular rods and rod bundles. These results indicate that the aragonite is apt to grow into rods and rod bundles in morphology (the characteristic morphology of the aragonite is mainly columnar or fibrous [17]) under the experimental condition, and the calcite is apt to form squares in morphology. The addition of ethylene glycol mainly achieves the controllable synthesis of the CaCO₃ by regulating the mass fraction of aragonite and calcite in the CaCO₃ sample to acquire the rod bundles.

During the synthetic process, the presence of alcoholic hydroxyl groups in the ethylene glycol generally accelerates the growth rate of CaCO₃ crystals while inhibits the conversion of CaCO₃ crystals into stable calcites [21]. The introduction of ethylene glycol changes the number of alcoholic hydroxyl groups as well as the viscosity of the reaction system, which has a successive effect on the acceleration of the growth rate of CaCO₃ crystal. When the ethylene glycol addition is low, the effect of the alcoholic hydroxyl groups in the system on suppressing the conversion of calcite is limited because of the relatively low concentration, thereby resulting in a high mass fraction of calcite in the CaCO₃ sample that performs cuboid structure. An excess of ethylene glycol addition may significantly increase the concentration of hydroxyl groups; however, the increased viscosity of the system is unfavourable to the growth rate of CaCO₃ crystals, which also leads to a high amount of calcite in the CaCO₃ samples (Table 2). In this case, elevating the reaction temperature generally decreases the viscosity of the system, thus expediting the growth rate of CaCO₃ crystal nuclei due to the accelerated diffusion rate of the system and depressing the conversion of CaCO₃ into calcite (Table 3). Herein, an opportune addition of ethylene glycol (30 mL) and a reaction temperature of more than 80 °C in our system is crucial to achieving the successful synthesis of uniform CaCO₃ rod bundles.

According to a Muffins–Sekerka interface stability theory (MS theory) [22], the driving forces of crystal growth at different orientations and sites lead to the variance in the crystal growth rate when the external conditions are unbalanced. Combining the MS theory for the crystal growth, we proposed a formation mechanism for the CaCO₃ rod bundles as shown in Figure 10. Due to the existence of ethylene glycol with high polarity in the aqueous solution, the plane crystal interface of CaCO₃ crystal

![FIGURE 8 XRD patterns of CaCO₃ samples prepared at different reaction temperatures](Image)

| Serial number | Reaction temperatures / °C | Mass fraction of aragonite / % |
|---------------|----------------------------|------------------------------|
| 1             | 50                         | 50.79                        |
| 2             | 60                         | 82.88                        |
| 3             | 70                         | 88.20                        |
| 4             | 80                         | 94.92                        |
| 5             | 90                         | 95.01                        |
FIGURE 9  FESEM images of CaCO₃ samples prepared at different reaction temperatures. (a) 50 °C; (b) 60 °C; (c) 70 °C; (d) 80 °C; (e) 90 °C

FIGURE 10  Schematic diagram of the formation process of CaCO₃ rod bundles

loses the stability followed by the generation of tiny branches at the interfacial convex sites. The uniform CaCO₃ rod bundles are eventually formed after the tiny branches grow into CaCO₃ rods.

4  |  CONCLUSION

To sum up, we present here the synthesis of CaCO₃ rod bundles on a large scale from carbide slag via a straightforward
extraction-precipitation process. The ethylene glycol serves as a crystal modifier generally promotes the regioselective growth of CaCO₃ crystal from polymorph to mono-crystal, leading to the formation of aragonite with a high mass fraction of more than 94.9%. The facile strategy developed here offers a guideline for the solid waste management and provides an avenue to fabricate other CaCO₃ crystal with fine-tuning morphologies and peculiar crystalline structure. Further work might be focused on studying the use of these unique CaCO₃ crystals in the fields of catalysis, pharmaceuticals, polymers, paper, inks etc.

CONFLICT OF INTEREST
The authors declare no conflict of interest.

Baojun Yang
Zongqi Shao
Dongxue Zhang
Bainian Wang

School of Chemistry and Chemical Engineering, Hefei University of Technology, No. 193 Tunxi Road, Hefei City, Anhui Province, Hefei, Anhui 230009, People’s Republic of China

Correspondence
Bainian Wang, School of Chemistry and Chemical Engineering, Hefei University of Technology, No. 193 Tunxi Road, Hefei City, Anhui Province, Hefei, Anhui 230009, People’s Republic of China.

ORCID
Bainian Wang https://orcid.org/0000-0002-0848-5781

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