

Precipitation of flaky moolooite and its thermal decomposition

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Abstract: Moolooite particles with flaky morphology were synthesized by mixing dilute solutions of copper nitrate and sodium oxalate in the presence of citric acid. Solution pH value, citric acid concentration, and stirring were found to have large effect on the shape of the precipitated particles. Under the stirring, the radial area of flaky moolooite particles was enlarged and extended to become a thinner and larger flake. This is ascribed to growth promotion caused by the selective absorption of citric ligands onto a particular crystalline surface of the moolooite particles. Flaky shape of the moolooite particles tended to become spherical and disappeared completely when decomposed under an Ar atmosphere, leading to the formation of large porous aggregated particles composed of many tiny nanosized copper crystals.

Keywords: copper oxalate; citric acid; nanocrystals; porous materials; thermal decomposition

1. Introduction

Copper particles with different sizes and shapes are used extensively in electronics [1–2], sensors [3], paints [4], and sterilization [5]. Various methods have been developed to prepare fine copper particles, such as aqueous reduction by hydrazine [6], ascorbic acid [7], formaldehyde [8], and other similar methods [9–12]. In order to satisfy various requirements of metal particles for real applications, fine particle tailoring principles and techniques have been intensively studied by many researchers [13–15]. The most common tailoring measures are performed in aqueous media by scrupulous controlling the precipitation conditions including reaction concentration of metal ions or precipitants, temperature, aging time, pH value, and polymer additives. Once the particles with special morphology are precipitated, their morphologies usually can be maintained by careful thermal treatment, and this has become a quite traditional technical method for the preparation of various fine particles. Therefore, shape-tailoring methods are frequently designed by focusing on the precipitation process, as indicated in this present study.

Copper oxalate is a common precursor in the preparation of CuO and Cu particles in many studies due to its ease of being controlled during the precipitation process and its in-

herent good crystallization. Bowen *et al.* [16] reported that flaky copper oxalate particles were formed by using acetate ions as the shape tuning additive, which can help tailor shape of the precipitated particles. This work suggests that a simple anion has the large effect on the shape variation of precipitated copper oxalate particles. As to our knowledge, work on the tailoring effect of polymers on the morphology evolution of copper oxalate is seldom reported. In this work, we investigated the special role of citric acid in the formation of flaky copper oxalate particles, and sequentially synthesized Cu particle products by thermal decomposition.

2. Material and methods

Citric acid (Aldrich) was used as the crystalline modifier and prepared to a concentration of 10 g/L as a stock solution. All the other chemicals were of analytical grade.

The preparation of copper oxalate particles was carried out in glass vessels according to the method reported in open references [17–19]. Aqueous solutions of Na₂C₂O₄ (0.1 mol/L) and Cu(NO₃)₂ (0.1 mol/L) were prepared as stock solutions. In a standard synthesis procedure, a solution of Na₂C₂O₄ (0.1 mol/L, 5 mL), Cu(NO₃)₂ (0.1 mol/L, 5 mL), and citric acid solution (10 g/L, 1 mL) was injected dropwise into 90 mL of water. The solution was then stirred

magnetically and the pH value was adjusted to 3.5. This gave a final CuC_2O_4 concentration of 5 mmol/L. This mixture was sealed in a vessel and stirred for 14 h before the precipitate was collected by centrifugation. The final concentration of CuC_2O_4 varied from 1 mmol/L to 10 mmol/L, and the solution pH value varied from 2 to 6. As the comparing, CuC_2O_4 samples were prepared with no citric acid or stirring, but with all the same other conditions. In order to compare the thermal decomposition of the obtained CuC_2O_4 , the samples were heated in an argon and air atmosphere, respectively. The obtained particles were characterized with various instruments.

The collected powder samples were observed by FESEM (Zeiss Supra55, Germany), HRTEM (Zeiss EM-109, Germany), XRD (Rigaku FEN-100, Japan), and TG/DSC (Netzsch STA-449, Germany).

3. Results and discussion

3.1. Characterization of precipitated particles

A series of precipitation experiments under different conditions were carried out and the typical particle samples are shown in Fig. 1. It can be seen that flaky particles were formed when citric acid was added as a surfactant; by comparison, without citric acid the precipitated particles were brick-shaped. Obviously, the role of citric ligands is essential to the formation of flaky copper oxalate particles. This may be due to the selective absorption of citric ligands onto

a particular facet of the copper oxalate crystal, inhibiting its growth in the normal direction, which ultimately results in the formation of a flake. It is very interesting to note that during the precipitation process, if without stirring, the precipitated particles were flaky but with a much smaller radius. This can be attributed to the improved diffusion of copper oxalate monomers under stirring which causes the flaky particles to grow much faster. Simultaneously, the liquid layer on the surface of nuclei particles was also thinner due to the stirring effect. It would be better for copper oxalate precursor monomers to diffuse and cross the liquid layer as well as deposition on the nuclei surfaces to promote growth. While if without stirring, the liquid layer of the nuclei crystal was much thicker and the monomers needed to cross a longer distance, therefore, the nuclei did not get sufficient precursors for growth and under the selective absorption of citric ligands onto the special facet of copper oxalate crystals, the smaller flaky particles would be obtained finally.

Compared with copper oxalate particles in the literature which are reported to be cubic or spherical, the particles prepared in this work indicates the great effect of citric ligands on the morphology of precipitated particles. Other common additives, such as polyethylene glycol (PEG) and polyvinyl pyrrolidone (PVP), were also tested but no flaky particles were obtained. Therefore, the formation of flaky shape can be explained by the coordination effect of copper ions and citric functional ligands, which has been elucidated in the preceding section.

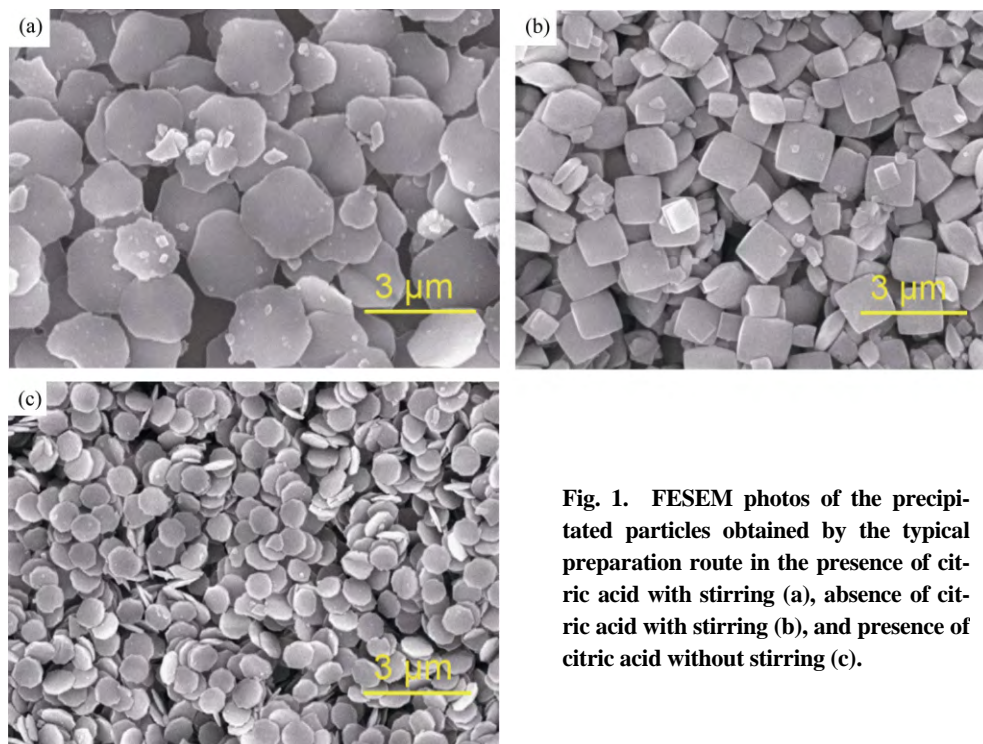


Fig. 1. FESEM photos of the precipitated particles obtained by the typical preparation route in the presence of citric acid with stirring (a), absence of citric acid with stirring (b), and presence of citric acid without stirring (c).

Fig. 2 shows the XRD results of the above mentioned precipitated particle samples. It can be seen that all the particles were copper oxalate hydrate, corresponding to mineral moolooite ($\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O}$, $0 < n < 1$). The crystalline size was evaluated (~ 95 nm, ~ 78 nm, ~ 90 nm) from the peak at 2θ around 20.3° using the well-known Scherrer equation, indicating that the precipitated particles in Fig. 1 were all polycrystalline. The sample in Fig. 1(a) was observed with HRTEM, as shown in Fig. 3, and it was found that the precipitated particles were formed by the aggregation of a number of tiny nanosized moolooite crystals.

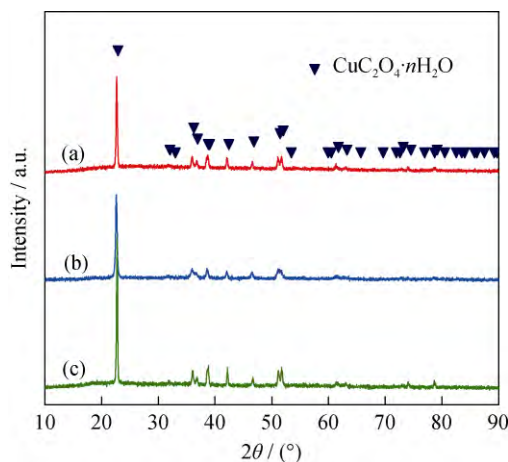


Fig. 2. XRD patterns of the precipitated particles obtained by the typical preparation route in the presence of citric acid with stirring (a), absence of citric acid with stirring (b), and presence of citric acid without stirring (c).

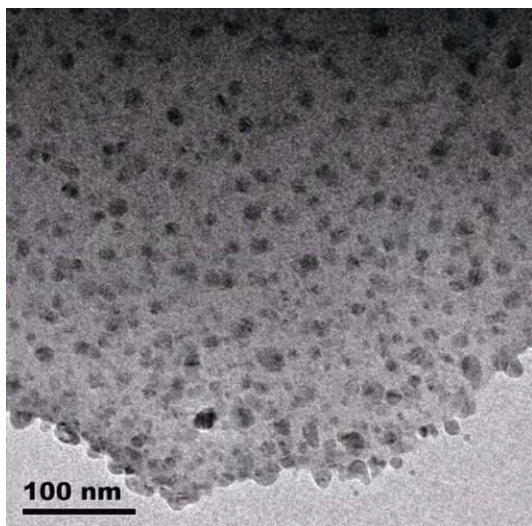


Fig. 3. HRTEM photo of copper oxalate particles obtained by a typical preparation route in the presence of citric acid with stirring.

3.2. TG/DSC analysis

Fig. 4 shows the TG/DSC results, conducted in flowing

air and Ar gas, respectively, from the samples in Figs. 1(a) and 1(b). It can be seen that the moolooite particle obtained in the presence of citric acid, decomposes more easily than that without citric acid. The complete decomposition temperatures were 300°C and 320°C in air, and 340°C and 380°C in Ar gas, respectively. Both the moolooite samples exhibited lower decomposition temperatures in air than in Ar. Obviously, the presence of the citric ligand plays a significant role in this process, and it probably causes the looser crystalline density of the moolooite crystals due to its introduction into the crystal lattice.

During the pyrolysis process, it can be found that the decomposition is easier for the copper oxalate particle samples prepared in the presence of citric acid. In flowing air, a sharp loss in mass occurs between 200°C and 300°C , which corresponds to the acute decomposition of copper oxalate with a mass loss of 50.16wt% and 47.60wt% for the two precipitated samples prepared in the presence and absence of citric acid, respectively. The decomposition can be written as follows: $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O} + 1/2\text{O}_2 = \text{CuO} + 2\text{CO}_2 + n\text{H}_2\text{O}$. For comparison, in Ar gas for the same above two precipitated samples, a sharp loss of mass occurs between 200°C and 400°C , which corresponds to the acute decomposition of copper oxalate with a mass loss of 53.72wt% and 52.10wt%, respectively. The decomposition in this case can be written as follows: $\text{CuC}_2\text{O}_4 \cdot n\text{H}_2\text{O} = \text{Cu} + 2\text{CO}_2 + n\text{H}_2\text{O}$. The exothermal peaks were both located at a decomposition temperature range much lower than that of the moolooite samples obtained without citric acid, which suggests that the citric acid role in thermal decomposition behavior is quite significant.

3.3. Characterization of decomposed particles

Fig. 5 shows the XRD pattern of the thermally decomposed product in Ar at 350°C , and it can be seen that a pure copper phase is obtained. Furthermore, the FESEM observation shows that nanosized copper tends to aggregate into larger particles with great porosity, and the original flaky moolooite shape disappears completely. This can be explained that the nanosized flaky moolooite particles have a large specific surface in a quite active energy state; therefore, they tend to shrink greatly at high temperature during the decomposition process, and transform into tiny spherical copper particles that further aggregate into larger particles with a porous structure. Therefore, because of the large specific surface area of the nanosized flaky moolooite particles, the final particle products had a spherical morphology which is beneficial for the reduction of active surface energy.

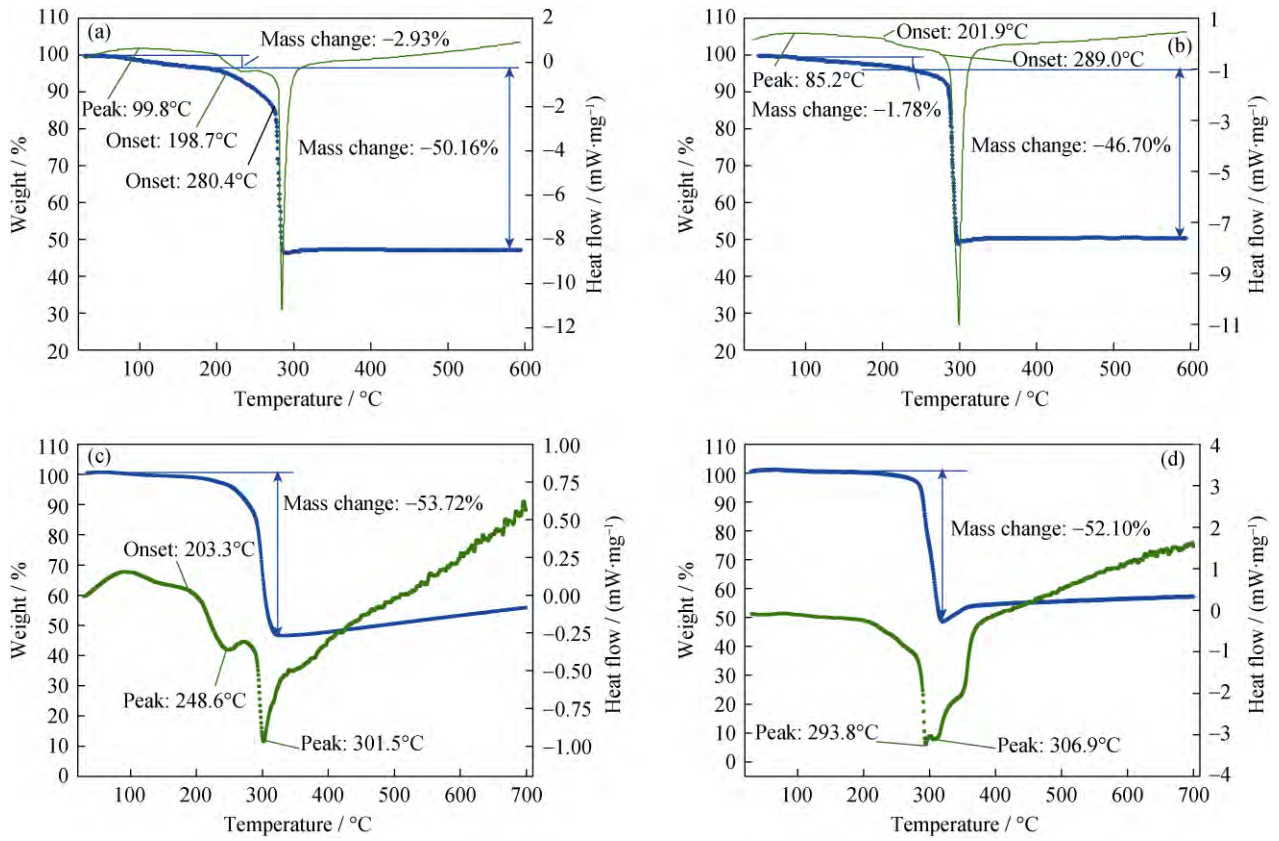


Fig. 4. TG/DSC curves of copper oxalate particles obtained by the typical preparation route in the presence of citric acid under (a) air and (c) Ar and in the absence of citric acid under (b) air and (d) Ar.

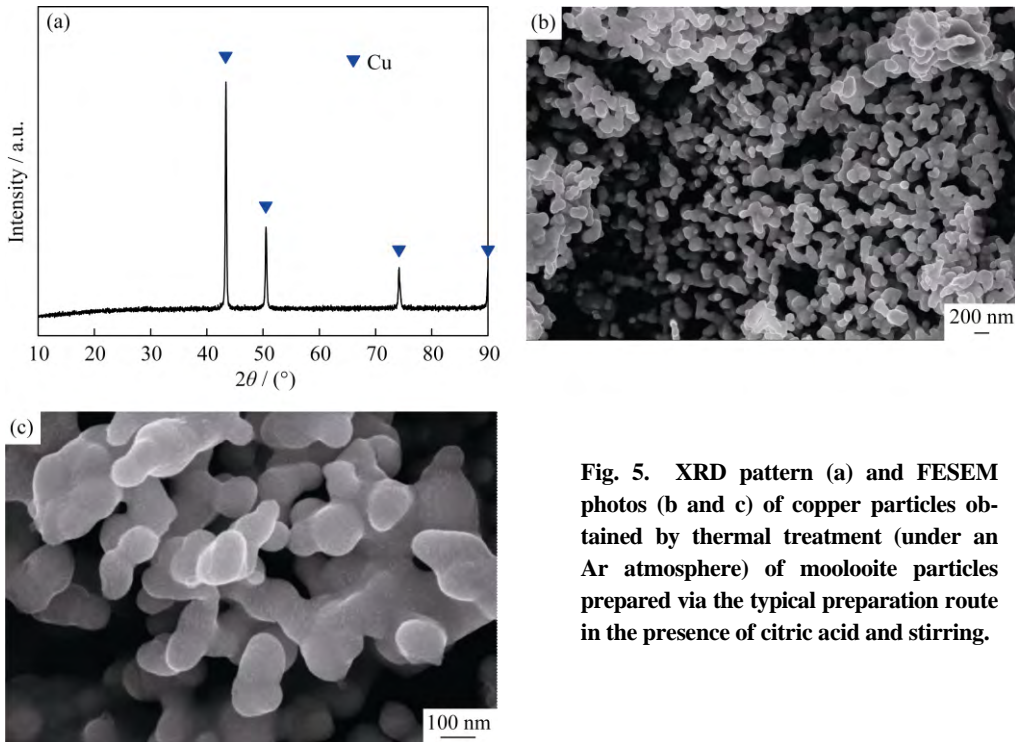


Fig. 5. XRD pattern (a) and FESEM photos (b and c) of copper particles obtained by thermal treatment (under an Ar atmosphere) of moolooite particles prepared via the typical preparation route in the presence of citric acid and stirring.

4. Conclusion

Monodispersed moolooite particles with flaky morphology were prepared by precipitation of dilute copper nitrate and sodium oxalate solutions in the presence of citric acid, and it was found that citric ligands had a significant effect on the formation of the flaky shape. The radial area of moolooite particles can be significantly enlarged by stirring. Pure copper nanoparticle aggregates with a porous structure were obtained by decomposition under an argon atmosphere.

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