

Composition and morphology of complicated copper oxalate powder

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Abstract: In $\text{Cu(II)-C}_2\text{O}_4^{2-}\text{-NH}_3\text{-NH}_4^+\text{-H}_2\text{O}$ system, complicated copper oxalate powders were synthesized by coordination-precipitation process with ammonium oxalate as precipitating agent. The composition and morphology of the powders were characterized by chemical analysis, X-ray diffraction (XRD), scanning electron microscopy (SEM), infrared spectroscopy (IR), and thermogravimetric and differential thermal analysis (TGA-DTA). The effects of temperature, copper ion concentration and pH value were investigated. The experimental results show that pure copper oxalate hydrate is prepared below a critical pH value of 6.0, whereas the powder turns to be a complicated copper salt combined with NH_3 over the pH value. Probable chemical formula, $\text{CuC}_2\text{O}_4 \cdot x(\text{NH}_3) \cdot y\text{H}_2\text{O}$ can be assumed, where x and y relate to experimental conditions. Technological parameters, such as temperature, initial copper concentration and solution pH value, have significant effects on particle size, morphology and dispersion of the powders. Powders with various morphologies, pie shape, spindle shape and rod shape, can be synthesized under certain technological conditions.

Key words: copper oxalate; preparation; coordination; morphology; composition

1 Introduction

Owing to copper powder with good surface activity and electrical conductivity, it is widely used as powder metallurgy material[1], friction and antifriction material[2–3], catalyst[4–6], conducting coat or film[7–9], electromagnetic shielding material[7], etc. The methods available for ultrafine copper powder preparation include gas-phase vapor method[10], electrolytic process[11], liquid phase reducing[12], and so on. ZHANG et al[13] reported that fibrous nickel powder was prepared by liquid phase precipitation and thermal decomposition method. Through a series of experiments, it is found that this method is also adapted to copper powder preparation. In contrast to the other methods, it is better for its simple process, low cost, controllable morphology and good quality of the products. By the method, once the powders are formed in the precipitation process, their basic characteristics, such as morphology, will be maintained. It is clear that the precipitation has great effect on the properties of the final product. In Ref.[14], the thermodynamic analysis was studied on preparation of special copper precursor powder with oxalate precipitation process in

$\text{Cu}^{2+}\text{-C}_2\text{O}_4^{2-}\text{-NH}_3\text{-NH}_4^+\text{-H}_2\text{O}$ system. The theoretical calculation results indicated that solution pH value and original reactant concentration had a great influence on ion species and their equilibrium concentrations in solution, as well as morphology of precursor powder. Therefore, it is well worth having a detail study on experimental process of precursor preparation. In this research, the synthesis of complicated copper oxalate powder was researched by coordination-precipitation process. The effects of the variable parameters in precipitation, such as temperature, reactant concentration and solution pH value, on the morphology, dispersion as well as the particle size of the powders were investigated.

2 Experimental

2.1 Synthesis process

Copper chloride solution and ammonium oxalate solution were prepared based on the requirements of stoichiometric ratio. All the solutions were elaborated by distilled water. The ammonium oxalate solution was heated to 30–70 °C and injected into the bulk copper chloride solution with peristaltic pump. Meanwhile, ammonia water was added to adjust and stabilize the

solution pH. After agitating and aging, the precipitate was washed with distilled water and ethanol, then filtered and dried in a vacuum drier at 100–120 °C for more than 12 h. Finally, the product powders were obtained.

2.2 Characterization

The structure and composition of as-prepared powders were measured with X-ray diffractometer (D/max-r A10 Type, Japan). Infrared (IR) spectra were recorded on a Nexus 470 spectrometer in the range of 4 000–400 cm^{-1} , and spectra were measured on KBr discs. The morphology, particle size and dispersion were characterized with JSM-5600LV scanning microscope.

3 Results and discussion

3.1 Chemical analysis of Cu^{2+} and $\text{C}_2\text{O}_4^{2-}$ in powder

The powders prepared at various pH values were chemically analyzed, and the molar ratios of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ are shown in Table 1. The molar ratios of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ are close to 1:1.

Table 1 Molar ratios of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ in powders prepared at various pH values

pH	5.5	6.4	6.8	7.5	8.2
$n(\text{Cu}^{2+})/n(\text{C}_2\text{O}_4^{2-})$	0.981	0.982	0.985	0.984	0.983

3.2 XRD analysis

Fig.1 illustrates X-ray diffraction patterns of the powders synthesized at different pH values. It can be found that all the five kinds of powders show crystal structure, and at pH 6.4, 6.8 and 7.5, XRD patterns of powders are nearly the same, which are significantly different from the other two. Compared with standard JCPDS card (PDF-21-0297), the powders prepared under the condition of pH 5.5 are proved to be $\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$;

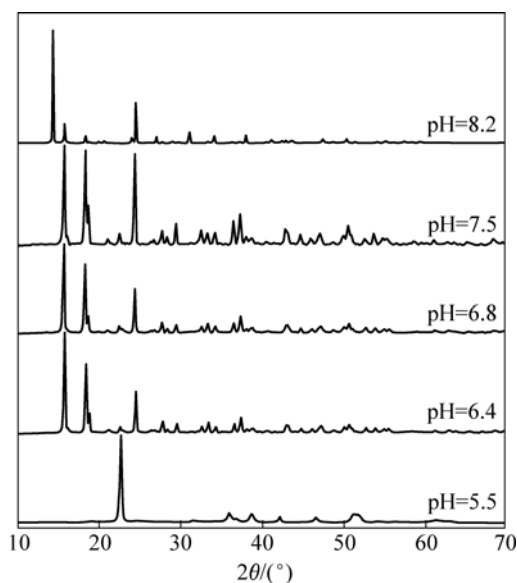


Fig.1 XRD patterns of powders prepared at various pH values

however, the other four patterns do not show any $\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ peaks, and also accord with none of the standard JCPDS cards at present. But from Table 1, the molar ratios of Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ are about 1:1, which suggests they are complicated copper oxalate instead of pure $\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

3.3 IR spectra of powders prepared at different pH values

IR spectra of powders prepared at various pH values are shown in Fig.2. On curve (a) of Fig.2, the band at 3 430 cm^{-1} is attributed to the symmetrical stretching vibration of hydrogen bond of $\text{C}_2\text{O}_4^{2-}$ ions ($\nu_{\text{s(OH)}}$ and $\nu_{\text{a(OH)}}$)[15]. A band at 1 662 cm^{-1} is due to stretching vibration absorption mode of $\text{C}_2\text{O}_4^{2-}$ ($\nu_{\text{as(C=O)}}$). Between 1 421 and 1 320 cm^{-1} , there are a weak band at 1 421 cm^{-1} and two strong bands at 1 363 cm^{-1} and 1 320 cm^{-1} , respectively, resulting from vibrations of $\text{C}_2\text{O}_4^{2-}$ ($\nu_{\text{s(C-O)}}$, $\nu_{\text{s(C-C)}}$ and $\delta_{(\text{O-C=O})}$). In the range of 823–506 cm^{-1} , a strong band at 823 cm^{-1} can be attributed to the vibration mode of $\text{C}_2\text{O}_4^{2-}$ ($\nu_{\text{s(C-O)}}$ and $\delta_{(\text{O-C=O})}$) and a strong one at 506 cm^{-1} originates from stretching vibration of Cu-O bond. Curve (b) differs from curve (a). The band at 3 430 cm^{-1} shifts and splits into two bands at 3 348 cm^{-1} and 3 285 cm^{-1} . The shoulder at 1 662 cm^{-1} splits into three shoulders at 1 714, 1 687 and 1 612 cm^{-1} . The bands at 1 714 cm^{-1} and 1 612 cm^{-1} can be attributed to the bending vibration of NH_3 ($\delta_{\text{a(HNH)}}$). Between 1 450 and 1 210 cm^{-1} , there are three stretching vibrations of $\text{C}_2\text{O}_4^{2-}$, and the shoulder at 1 421 cm^{-1} disappears and a band at 1 271 cm^{-1} appears. In the range of 823–506 cm^{-1} , the bands at 823 cm^{-1} and 506 cm^{-1} are still the same as curve (a), except a weak stretching vibration of $\text{C}_2\text{O}_4^{2-}$ at 666 cm^{-1} . Contrasting with curve (b), curves (c) and (d) are basically the same, and the only difference is the gradual enhancement of vibration of NH_3 . It can be drawn a conclusion that as-prepared powders are $\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ when pH is 5.5; but as pH value increases,

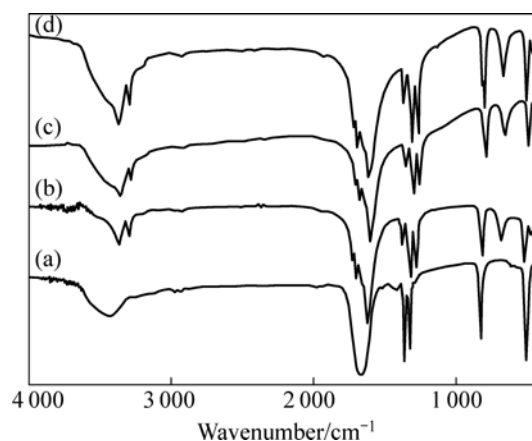


Fig.2 IR spectra of powders prepared at various pH values: (a) pH=5.5; (b) pH=6.4; (c) pH=7.5; (d) pH=8.2

more NH_3 begins to react with powders, thus the composition of powders consist of ammonia and copper oxalate instead of the pure copper oxalate.

IR spectra analysis confirms that NH_3 molecule exists in the powders when solution pH value is over 6.4. In addition, Cu^{2+} to $\text{C}_2\text{O}_4^{2-}$ molar ratio is close to 1:1, thus the chemical formula, $\text{CuC}_2\text{O}_4 \cdot x(\text{NH}_3) \cdot y\text{H}_2\text{O}$, can be assumed, and x and y relate to experimental conditions.

3.4 Thermal stability of as-prepared powders

TGA/DTA curves of samples prepared at different pH values are described in Fig.3. From Fig.3(a), it can be

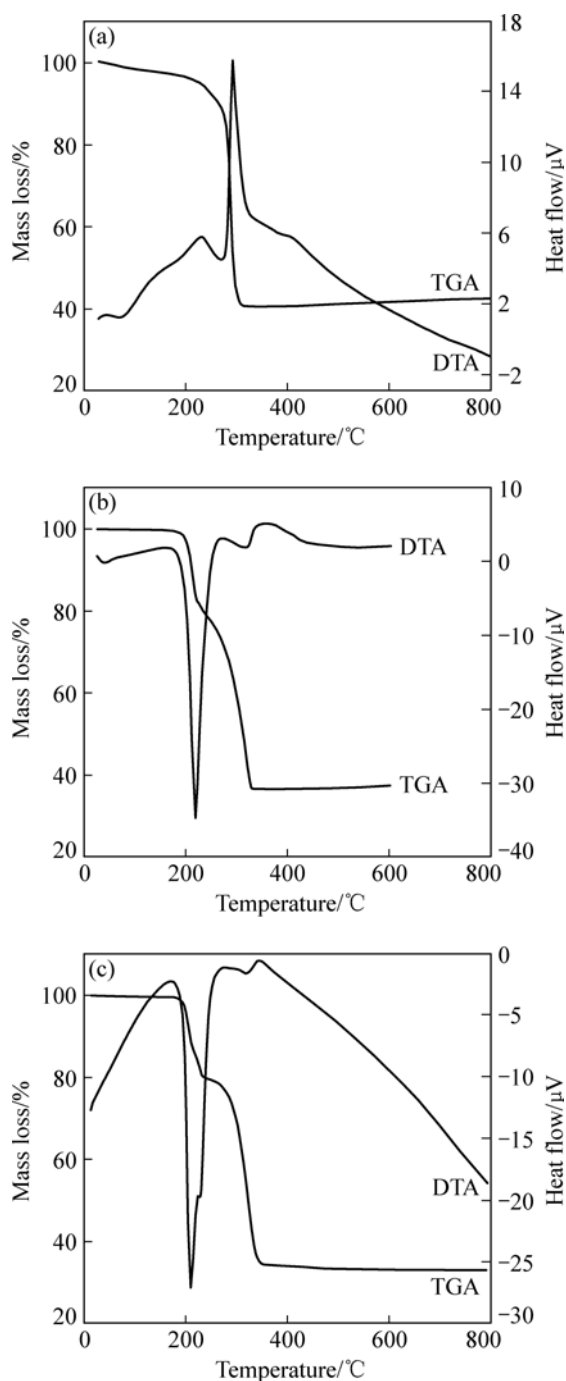


Fig.3 TGA/DTA curves of powders prepared at various pH values: (a) pH=5.5; (b) pH=6.8; (c) pH=8.2

seen that there are two endothermic peaks at 90 °C and 270 °C, and one large exothermic peak at 290 °C on DTA curve, respectively corresponding to elimination of adsorptive and crystal water around 90 °C, liberation of CO by decomposition of copper oxalate at 270 °C, and liberation of CO_2 and partial reduction of CuO by CO at 290 °C. Concerning Figs.3(b) and (c), the TGA/DTA curves are almost the same, showing that powders continually lose mass as the temperature rises. Around 210 °C, there is a sharp endothermic peak on the DTA curve, meaning the elimination of the $x\text{NH}_3$ from the $\text{CuC}_2\text{O}_4 \cdot x(\text{NH}_3) \cdot y\text{H}_2\text{O}$; in addition, there exists a relatively weak endothermic peak at 230 °C, indicating the elimination of y crystal water from $\text{CuC}_2\text{O}_4 \cdot x(\text{NH}_3) \cdot y\text{H}_2\text{O}$. Due to the over-close distance between two peaks, they nearly overlap with each other. Meanwhile, on TGA curves, the two peaks have a total mass loss of 19.46%. Between 300 and 350 °C, there is a weak endothermic peak with mass loss of 45.57% due to the decomposition of CuC_2O_4 .

3.5 Effects of technological conditions on particle size and morphology of powders

3.5.1 Effect of temperature

With the other conditions being constants, the temperature in precipitation has significant effect on the morphology and particle size of the powder. It can be seen from Fig.4 that spindle-shape plate aggregation powder is synthesized when pH value is controlled at 6.8. At relatively low temperature, for example, 30–50 °C, the size of obtained particles is small but non-homogeneous, and there exist lots of single spindle-shape particles (see Figs.4(a) and (b)). With the rise of temperature, heat motion in the system intensifies, meaning much more opportunities of particle encounter. Thus, the length, width and thickness of particle increase, although the length begins to shorten over a certain temperature. It is known that the morphology of crystal is eventually determined by the relatively competitive growth of the different crystal face orientation. The fast growing crystal face will certainly disappear and the slow growing crystal face may appear gradually. The change of the physicochemical condition may lead to the change of the unit structure pattern of the crystal growth; so the morphology of the particles may be different. The effect of the temperature is finally on the nuclei formation and growth because the increase of the temperature is beneficial for lowering the viscosity and increasing the diffusion of ions, and promotes the rate of crystal growth. In this system, the increase of temperature accelerates the growth rate of diametrical crystal faces much more than axial crystal faces. So, the axial crystal faces gradually appear (see Fig.4(d)).

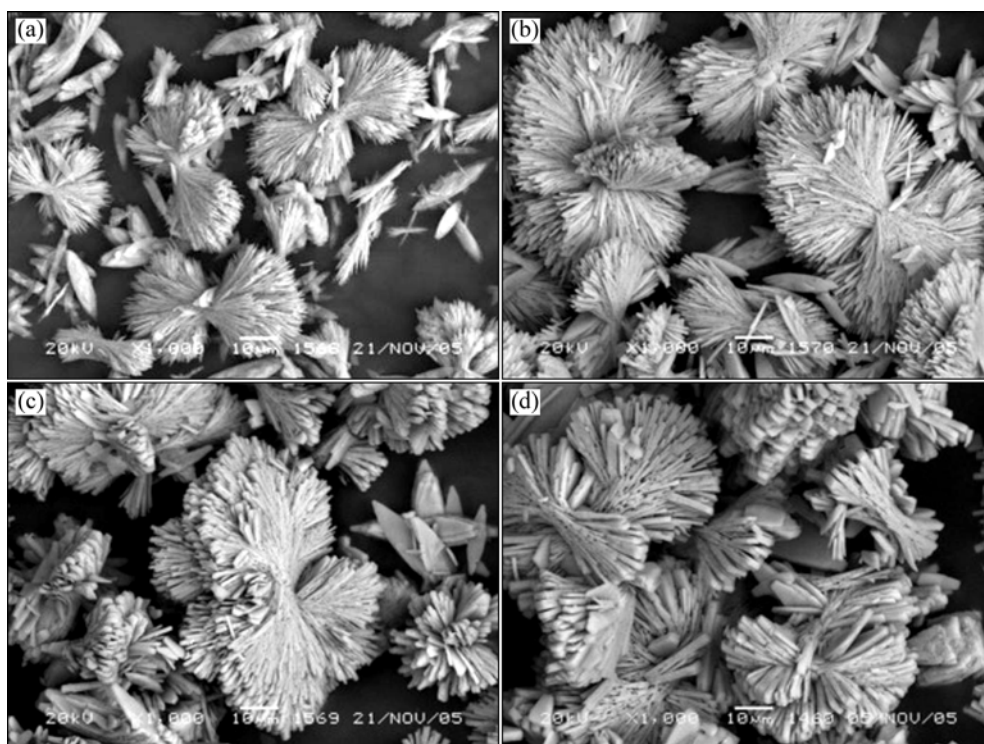


Fig. 4 SEM images of powders prepared at various temperatures at pH 6.8: (a) 30 °C; (b) 50 °C; (c) 60 °C; (d) 70 °C

3.5.2 Effect of initial reactant concentration

In the system, Cu^{2+} reacts with $\text{C}_2\text{O}_4^{2-}$ at chemical stoichiometry of 1:1. In order to improve the precipitation rate of Cu^{2+} , 1.1 times theoretical dosage of $\text{C}_2\text{O}_4^{2-}$ is used. Under the same conditions of temperature and pH value, the change of the initial reactant concentration has obvious impact on the morphology of powder particles. When pH value is controlled at 6.8, the results obtained at different reactant concentrations are shown in Fig.5. It can be found from the results that, the concentration of the copper ions exerts significant influence on the morphology of the powder particles, that is, due to the increase of $c(\text{Cu}^{2+})$, the width of particle enlarges, accompanied with reveal of crystal faces in axial orientation. When $c(\text{Cu}^{2+})$ equals 0.4 mol/L, the particles show the morphology of aggregation of spindle-shape plate as described above. When $c(\text{Cu}^{2+})$, nevertheless, lowers to 0.1 mol/L, the specific morphology of the particles turns to be aggregation of rectangle-shape plate with incremental thickness. When $c(\text{Cu}^{2+})$ exceeds 0.6 mol/L, some flake particles with large width emerge. When $c(\text{Cu}^{2+})$ reaches 1.0 mol/L, the particles show poor crystallinity, even abruption. It is well known that in classical crystallographic theory, the formation of powder particles embraces two processes, nucleation and crystal growth. In lower copper concentration, the degree of saturation in solution is relatively low, meaning slower

nucleation rate. In this case, epitaxial and superficial growth of crystal predominates, which contributes to perfect crystallinity. On the contrary, exorbitant copper concentration will lead to explosion of nuclei and losing control of crystal growth. Therefore, proper initial copper concentration is necessary.

3.5.3 Effect of solution pH value

In the experiment, in order to minimize the introduction of impurities into solution, ammonia water was used to adjust solution pH value. As seen in Fig.6, at different pH values, the powders show essential changes in particle size and morphology. When pH is 5.5, the pie-shaped particles are obtained; however, when pH ranges from 6.4 to 7.5, the spindle-shaped plate aggregation particles are produced; furthermore, when pH is above 8.2, rod-shaped particles are yielded. From the results, it is indicated that when pH increases to a critical value, the behavior of crystal growth changes obviously, from pie shape, through spindle shape, to rod shape finally. From the results of XRD patterns, chemical analysis and infrared spectrum analysis, it is confirmed that under the condition of low pH value, i.e. 5.5, the as-prepared powders consist of copper oxalate hydrate, and at higher pH value the powders convert to complicated copper oxalate powders combined with NH_3 . The higher the pH value is, the more the ammonia exists in powder. Thus, it is reasonable to conclude that ammonia combined in powder plays a decisive role in

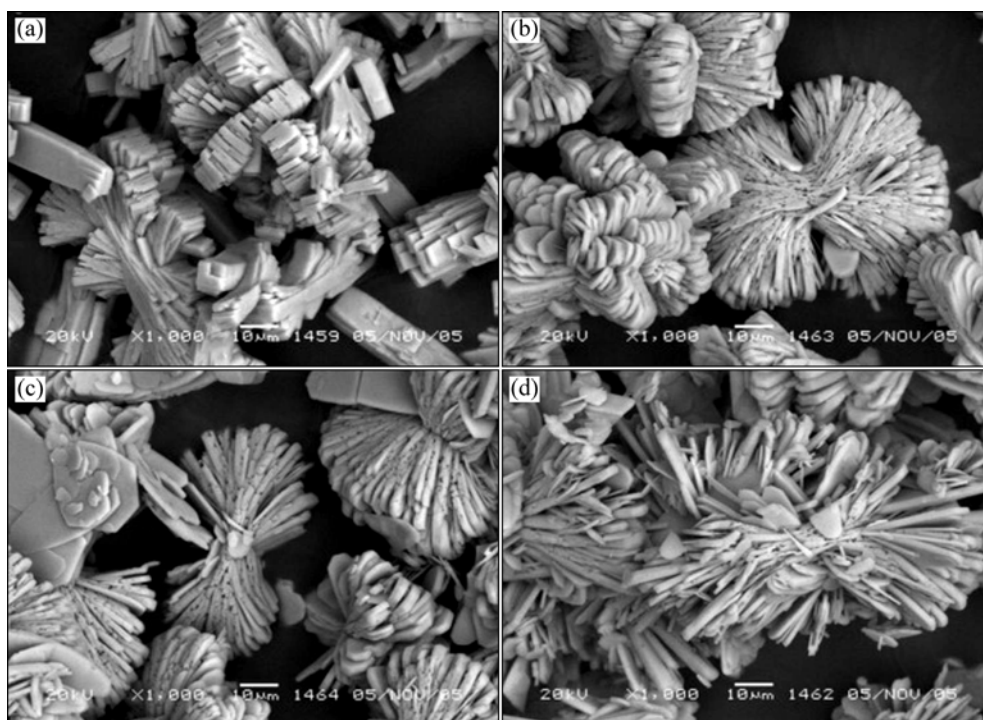


Fig. 5 SEM images of powders prepared at various copper ion concentrations at pH 6.8: (a) $c(\text{Cu}^{2+})=0.1$ mol/L; (b) $c(\text{Cu}^{2+})=0.4$ mol/L; (c) $c(\text{Cu}^{2+})=0.6$ mol/L; (d) $c(\text{Cu}^{2+})=1.0$ mol/L

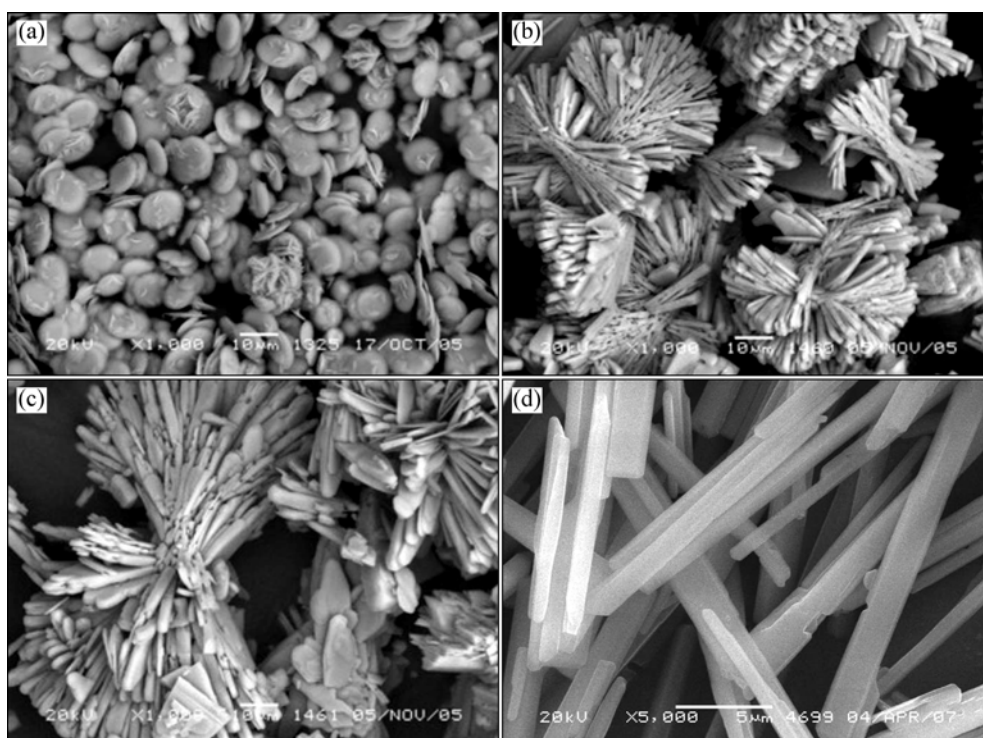


Fig.6 SEM images of powders prepared at various pH values: (a) pH=5.5; (b) pH=6.4; (c) pH=7.5; (d) pH=8.2

morphology of crystal growth.

4 Conclusions

- 1) The powders synthesized by coordination-

precipitation process have crystal structure. From the results of XRD patterns, chemical analysis, IR spectrum and TGA/DTA curves, with the increase of solution pH value, their phase changes from $\text{CuC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ to complicated copper oxalate combined with NH_3 .

Furthermore, the content of NH_3 increases with the rise of pH. The probable chemical formula, $\text{CuC}_2\text{O}_4 \cdot x(\text{NH}_3) \cdot y\text{H}_2\text{O}$, can be assumed, and x and y relate to experimental conditions.

2) Technological parameters, such as temperature, initial copper concentration and solution pH value, have significant effects on particle size, morphology and dispersion of powder. Controlling technological conditions, powders with various morphologies, pie shape, spindle shape and rod shape, can be synthesized.

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