



MICROWAVE ASSISTED SYNTHESIS OF COBALT PHOSPHATE NANOPARTICLES

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The uniform cobalt phosphate nanoparticles were successfully synthesized by microwave radiation. The effects of microwave irradiation power and reaction time on the treatment process were investigated. The products synthesized were analyzed by field emission scanning electron microscopy, X-ray powder diffraction, Fourier-transform infrared spectroscopy, thermal gravimetric analyses and dynamic light scattering. In this research, the products were cobalt phosphate phase with nanoparticles over the ranges of 60-80 nm. The data revealed that the nearly spherical particle size decreased with increasing irradiation power. The cobalt phosphate nanoparticles were formed after 10 min of microwave irradiation.

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Introduction

Nanomaterials are defined as materials which length less than 100 nm at least in one dimension. When the materials enter into nanoscale, they will show special properties which were different from the bulky materials. Nanomaterials have special properties including quantum size effect, surface effect and macroscopic quantum tunneling effect.^{1,2} With these physicochemical features, nanomaterials have been used as electronic components, paint, sports equipment, cosmetics and food additives.³ Cobalt phosphate ($\text{Co}_3(\text{PO}_4)_2$) was found as violet pigment used in chemical industry in 1895. $\text{Co}_3(\text{PO}_4)_2$ can be used as catalyst in the oxidation of water in the presence of sun light and for the selective reduction of NO with C_3H_6 or CH_4 .⁴ The modification with an appropriate amount of $\text{Co}_3(\text{PO}_4)_2$ could greatly enhance the activity for photoelectrochemical water oxidation of TiO_2 .⁵ The addition of $\text{Co}_3(\text{PO}_4)_2$ in Fe_2O_3 enhance the photocatalytic activity of composite electrode for water photooxidation.⁶ The properties included catalytic activity, conductivity and electron affinity of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were improved by the nanostructure.⁷ $\text{Co}_3(\text{PO}_4)_2$ nanoparticles with novel properties have broad application prospects in battery cathodes usage and catalytic applications.⁸

The traditional preparation method of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles is the coprecipitation synthesis.⁹ Conventional coprecipitation synthesis can yield larger quantities, but it is difficult to achieve a narrow particle size distribution when the particle size less than 100 nm. It also has high reaction temperature, poor reactivity, particle aggregation, broad size distribution and other disadvantages.¹⁰ Microwave radiation technology is widely used to prepare high purity nanoparticles with narrow particle size distribution.

Microwave heating has been known since the early 1940s, and has been used in preparative chemistry and material synthesis since 1986.¹¹ Compared with the traditional heating method, microwave heating is an internal heat method which has unique features such as fast and uniform heating, no temperature gradient, short reaction time, and high reaction rate.¹² This is beneficial to the formation of uniform nanomaterials. For example, uniform barium carbonate nanoparticles were successfully synthesized using alkaline earth metal nitrate and sodium carbonate in ethylene glycol by a cyclic microwave radiation.¹³

In this study, $\text{Co}_3(\text{PO}_4)_2$ nanoparticles with different size were synthesized by microwave irradiation method and the influence of microwave power, reaction time on the size control of nanoparticles were investigated.

The synthesized $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were characterized using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), fourier transform infrared spectroscopy (FTIR), Thermal gravimetric (TG), differential thermal analyse (DTA) and dynamic light scattering (DLS). The results showed that the particle size could be tuned simply by adjusting the experimental parameters.

Experimental

Chemicals

All the chemicals used in this experiment were analytical grade materials and used without further purification. Cobalt sulfate heptahydrate ($\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, $\geq 99\%$), sodium dodecylbenzene sulfonate (SDBS, $\text{C}_{18}\text{H}_{29}\text{NaSO}_3$, 99%), sodium phosphate monobasic dihydrate ($\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, $\geq 99.0\%$) and urea (CON_2H_4 , $\geq 98\%$) were purchased from Aladdin Chemical Reagent. Deionized water was used throughout the reactions. All glasswares were washed with dilute nitric acid (HNO_3) and distilled water, then dried in hot air oven.

Synthesis of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles

The $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were synthesized as following process. 100 ml of 3 mM $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$, 3 mM $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$, 0.3 mg of $\text{C}_{18}\text{H}_{29}\text{NaSO}_3$ and 6 mg CON_2H_4 were mixed in a beaker to get an aqueous solution. The solution was transferred into a 200 ml beaker and heat-treated in a microwave oven (Galanz 800 W) for different time periods. Then the reactor device was taken out and cooled with water. After the reaction, the resultant product was separated by centrifugation (3000 rpm, 5 min) and washed repeatedly using water and anhydrous ethanol. Then the wet precipitate was dried at 100 °C in an oven for 2 h.

Characterization of nanoparticles

XRD was performed on an X-ray diffractometer employing Cu-K α radiation with 40 kV and 50 mA (D8 Advance, Bruker, Germany). The typical bonds were detected by fourier transform infrared spectroscopy (Nicolet 380, Thermo, USA). The FTIR spectra obtained using the improved KBr pellet method by grinding down the resin beads prior to recording. Thermal gravimetric (TG) and differential thermal analyses (DTA) were carried out in TG 209F3 instrument (TG 209F3, Netzch, Germany). A known mass of the sample was heated in a silica crucible at a constant heating rate of 10 °C min⁻¹ operating in nitrogen atmosphere with a flow rate of 40 mL min⁻¹ from 25 to 700 °C and mass loss per time and temperature increment were recorded. The morphology and size of synthesized $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were measured by FE-SEM (JSM-7500F, JEOL, Japan). A minute drop of nanoparticles solution was cast on to a carbon-coated copper grid and subsequently drying in air before transferring it to the microscope. The size distribution of the nanoparticles in medium was evaluated by DLS (Delsa Nano C, Beckman, USA). Data were analyzed based on six replicated tests.

Results and discussion

Effect of microwave power

The phase composition and structure of obtained samples at different microwave power were examined by XRD (Fig. 1). The reaction time was 15 min. All diffraction peaks can be indexed to the pure monoclinic phase of $\text{Co}_3(\text{PO}_4)_2$ which belonging to space group $P21/n$ with lattice constants $a = 7.556 \text{ \AA}$, $b = 8.371 \text{ \AA}$ and $c = 5.064 \text{ \AA}$ (JCPDS No. 01-077-0224). No other byproducts can be detected. The intensity of diffraction peaks increased along with increasing irradiation power. This indicated that crystalline phase developed more complete at higher microwave power. Meanwhile, when the irradiation power increased, the width of diffraction peaks increased slightly. This indicated that the particle size decreased slightly along with increasing irradiation power. The above results were also in accordance with the SEM observation (Fig. 4).

FTIR analysis

The FTIR spectra of the synthesized $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were shown in Figure 2. The triply degenerated asymmetric stretching and bending vibrations

of PO_4^{3-} were at 1030 and 570 cm^{-1} . The triply degenerated asymmetric stretching and bending vibrations of PO_4^{3-} were at 1030 and 570 cm^{-1} . The Co-O peaks were at 854 and 703 cm^{-1} . The emergence of the absorption peak of the Co-O and PO_4^{3-} shows that $\text{Co}_3(\text{PO}_4)_2$ nanoparticles have been formed. The peaks at 3000~3500 and 1627 cm^{-1} corresponded to the remaining water.

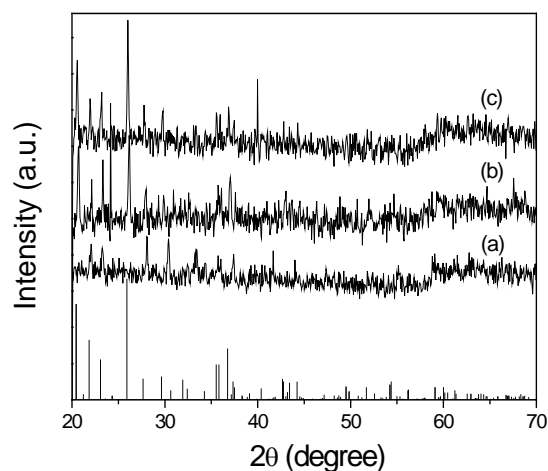


Figure 1. XRD patterns of product obtained at different microwave power. (a) 200 W (b) 500 W (c) 800 W

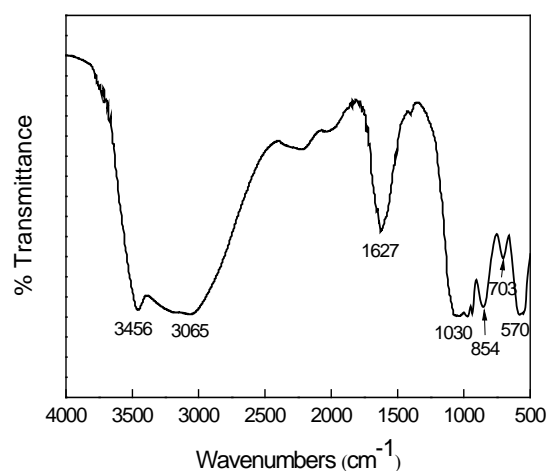


Figure 2. FTIR spectra of sample synthesized by microwave synthesis method.

Thermal gravimetric analysis

TG and DTG curves of the $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were shown in Figure 3. Two weight losses which corresponding to the removal of physisorbed and interlayer water were observed. The physisorbed and interlayer water molecules which are loosely bound and are mobile that they can be removed by heat treatment below 200 °C. The DTG curve provides more detailed information about the decomposition process. It is possible to distinguish perfectly two peaks in the region below 200 °C, corresponding to the removal first of physisorbed and then of interlayer water. The intensity of the two peaks could be related to the low crystallinity of the compound. It should be noted that the final weight is around 23.4% of the initial weight. The DTA curve of the $\text{Co}_3(\text{PO}_4)_2$ nanoparticles showed two endothermic peaks corresponding to the above mentioned weight losses.

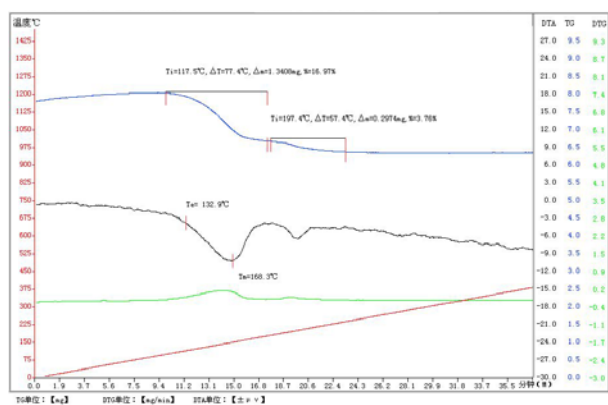


Figure 3. TG and DTG curves of the $\text{Co}_3(\text{PO}_4)_2$ nanoparticles.

Effect of reaction time

XRD spectra of the $\text{Co}_3(\text{PO}_4)_2$ nanoparticles prepared at different reaction time were shown in Figure 4. The microwave power was 800 W. The $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were formed after 10 min of microwave irradiation (Figure 4b). The corresponding SEM micrograph showed that $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were almost spherical and particle size was about 60 nm (Fig. 5c). The precursors have been converted to $\text{Co}_3(\text{PO}_4)_2$ when the reaction time was 10 min. The intensity and width of XRD diffraction peaks have no obvious change with extension of microwave irradiation time. This indicated that the particle size remains constant with different reaction times. It may be due to the nucleation and crystallization rate can be greatly accelerated by microwave irradiation method. So the particle size would not change obviously with the extension of reaction time. The above results were also in accordance with the SEM observation (Fig. 5c and 5d). Particle size estimated by XRD was shown in Table 1. The $\text{Co}_3(\text{PO}_4)_2$ average crystallite size was calculated using Scherrer equation ($R = 0.9\lambda/B\cos\theta_B$), where R is the average particle size (\AA), B is the width of the peak at half the peak height (radians), λ is the X-ray wavelength (nm), and θ_B is the Bragg angle ($^\circ$).

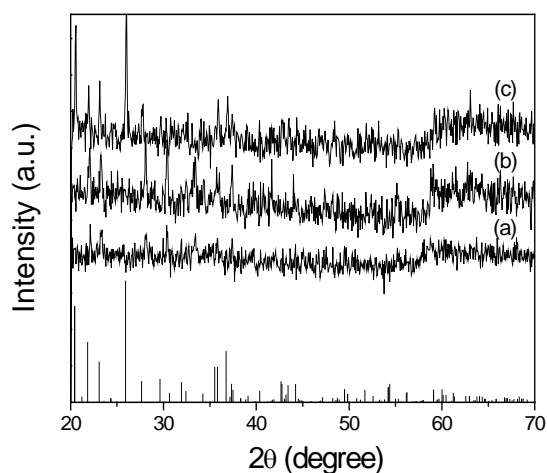


Figure 4. XRD patterns of product obtained from different reaction times. (a) 5 min (b) 10 min (c) 15 min

Table 1. Particle size as estimated from XRD and SEM measurements.

Sample	Microwave power, W	Reaction time, min	Size from XRD, nm	Size from SEM, nm
1	500	10	81	85
2	500	15	78	80
3	800	10	62	65
4	800	15	57	60

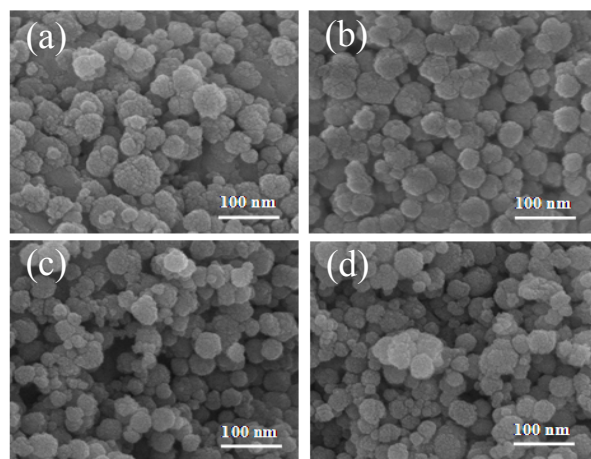


Figure 5. SEM images of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles obtained from different reaction times and microwave powers. (a) 10 min, 500 W (b) 15 min, 500 W (c) 10 min, 800 W (d) 15 min, 800 W

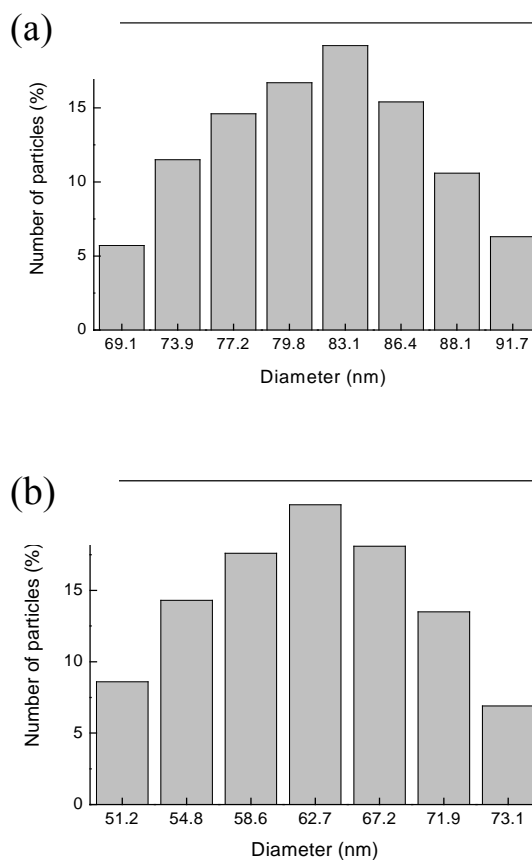


Figure 6. Size distribution of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles in water measured by DLS. (a) 15 min, 500 W (b) 15 min, 800 W

DLS analysis

The SEM images provided information on the primary size of nanoparticles, however, it could not provide information on whether the nanoparticles existed in single or aggregated forms in the culture medium. The size distribution in the culture medium, therefore, was investigated using a DLS method, which showed that the average size of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles in the culture medium were 83.5 ± 11.2 nm and 62.7 ± 9.4 nm, respectively (Fig. 6). The DLS analysis showed that the $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were homogeneously dispersed in culture medium. The fluid dynamics size of $\text{Co}_3(\text{PO}_4)_2$ nanoparticles which measured by DLS was in agreement with the primary size obtained by SEM.

Conclusions

In summary, quasi-spherical $\text{Co}_3(\text{PO}_4)_2$ nanoparticles were synthesized successfully using microwave irradiation method. Average size of the $\text{Co}_3(\text{PO}_4)_2$ nanoparticles was tunable by simply changing the microwave power and reaction time of the reaction.

The results of characterization showed that the particle size decreased along with increasing irradiation power in the formation of the nanoparticles. $\text{Co}_3(\text{PO}_4)_2$ nanoparticles with average diameter 80 nm for 500 W and 60 nm for 800 W were highly stable. XRD pattern showed that pure nanostructures with high crystallinity had been made.

Acknowledgments

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