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Solid-state chemical synthesis and characterization of nanocrystalline tartaric acid cerium rare earth compound under ultrasonication

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ABSTRACT

Under near ambient temperature and ultrasonication, the use of different cerium salt, respectively, with $C_4H_6O_6$ (tartaric acid) under solid state chemistry reactions, the synthesis of nano rare earth metal complexes of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) crystals was formed. The solid phase was characterized by powder X-ray diffraction (XRD) and electron diffraction (ED). The particle size, its distribution, and morphology of the prepared nanocrystallite were observed by transmission electron microscopy (TEM). The results show that particle sizes are relatively uniform, the morphology of the crystal is spherical, the average particle diameter is about 30 nm, and the yield rate is approximately 87.6%. Furthermore, during the synthesis, the solid-state reaction conditions including raw materials, matching proportion of reactants, additions of inert substance, addition of trace solvents, surfactants and porphyrization time, all have some influence on the morphology, particle size and size distribution of the final products. During the synthesis of the cerium succinate nanocrystallites, the solid state reaction conditions such as changing reactant, matching proportion of reactant, adding inert substance, joining a little solvent or surface active solvent and grinding at different times may influence morphology, particle size and the size distribution of final products.

KEYWORDS

Tartaric acid cerium nanocrystallite; Rare earth compound; Supersonic wave; Solid-state synthesis; Characterization.

INTRODUCTION

Nanocrystalline material has small size effect, quantum size effect, volume effect, surface effect and macroscopic quantum tunnel effect. It exhibits excellent characteristics in mechanics, catalysis, optics, electrics, magnetics, acoustics, calorifics, superconducting technology, chemical and biological activity, and so on. It also has high practical value in national defense, electronics, chemical industry, nuclear technology, metallurgy, astronautics, light industry, biological and medical industry. Recently it has become a foundation for developing special materials and has been active in the fields of physical, chemical and materials science research[1-5]. The study on the solid-state chemical reaction under ambient temperature and near ambient temperature has made great progress in recent years. The preparation of nanocrystallite generally requires: clean surface, controllable particle shape, size distribution that prevents particle agglomeration, easy collection, better stability and high productivity. The solid-state chemical reaction method can meet these needs and it is easy to operate with advantages of simple processes such as synthesis, high yield, high selectivity, uniform particle size distribution, controllable size and less pollution. It can prevent or reduce the phenomenon of agglomeration of the liquid phase and the phenomenon of particle agglomeration caused by intermediate step and high-temperature reaction, The solid-state chemical reaction process consists of four steps: diffusion-reaction-nucleation-growth. When the nucleation rate is greater than the nucleus's growth speed, it is beneficial to the formation of nanocrystallite. But if the nucleus's growing rate is greater than the nucleation rate, a lump crystal forms[6-10].

Tartaric acid cerium is an important rare earth compound with practical mechanical properties and lumkinescent properties. It is of vital significance to the method of solid-state synthesis in order to produce nanomaterials. This paper discusses the application or the solid-state chemical reaction to synthesize the nanocrystalline tartaric acid cerium under near ambient temperature and ultrasonication. With characterization and observation of the solid phase, particle size and morphology performed through powder X-ray diffraction (XRD), transmission electron microscopy (TEM) and electron diffraction (ED). It also discussed, the factors which the influence to the final product such as types of reactant, changing the proportions of reactant, addition of inert substances, mixing trace solvent or surfactant and time of porphyrizing[11-16].

EXPERIMENTAL

The experimental reagents were all analytically pure. Composing experiment regents are all the analytical purity baking 5.0 mmol $Ce(Ac)_3 \cdot 3H_2O$ and 15.0 mmol $C_4H_6O_6$ (tartaric acid) to grind in the agate pot with intrared light during grinding, the temperature is about 35~40°C, with the operate of ultrosonic, to wash the lomposing 3 times with distilled water, and then wash 2 times with alcohol, drying, finally the nanocrystlline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium). The processes was repeated three separate times using $Ce(NO_3)_3 \cdot 6H_2O$, $Ce_2(SO_4)_3 \cdot 9H_2O$, $CeCl_3 \cdot 7H_2O$ as the reactant in place of $Ce(Ac)_3 \cdot 3H_2O$. During each synthesis, the types of factors influencing the final product under different solid-state reaction conditions such as reactant, changing the proportions of reactant, addition of inert substances, mixing of trace solvent or surfactant and time of porphyrizing was also observed.

The solid phase was characterized by powder X-ray diffraction (XRD) and electron diffraction (ED). The particle size and its distribution and morphology of the prepared nanocrystallite were observed by transmission electron microscopy (TEM). The XRD spectra adopted Cu target in Rigaku D/Max-RA X-ray powder diffraction instrument, scanning with Be-window color filter and graph monochromator. The scanning speed was $4^0.min^{-1}$; the scanning interval was $5^0 <= 2\theta <= 60^0$; tube

voltage was 40 kV. The constants and powers for each test were the same. The TEM and ED patterns were obtained by utilizing a Japanese electronic type of JEM-200 CX transmission electric microscope at an accelerated voltage of 160 kV and an amplification of one hundred thousand times.

RESULT AND DISSCUSS

TABLE 1 shows the XRD patterns of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) nanocrystallite synthesized according to the conditions of No.16 in TABLE 2. Results of the synthesized $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) appears the XRD pattern of analytically pure $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) and the standard XRD pattern of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) from JCPDS card, and which has no impurity peaks. However, the diffraction peaks of the synthesized product were significantly widened and conspicuously weaker. According to X-ray polycrystal diffraction theory, the widening of the peak diffraction is because of the superrefining of the particle size. This indicates that the particle size of the synthesized $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is a single phase, ultrafine particle. According to the width of the peaks of the XRD pattern, and utilizing the formula of scherrer, the crystal's average particle size was calculated to be 30 nm. The particle size of the product is determined by the relative magnitude of the nucleation speed and the crystal nucleus's growing speed.

Results indicate that this condition enables the attainment of smaller nanocrystallites at ambient temperature, the nucleation speed is quicker than that of the nucleus's growth. Figure 1 shows the ED pattern of this same sample (synthesized according to No.16 in TABLE 2). The result shows that the round line of the diffraction is clear and is the result of multicrystal diffraction. Calculation of the d value (TABLE 1) of the corresponding diffraction, it shows that the product is the multicrystal $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium). Figure 2 shows the TEM result of the sample. The shape of the nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is approximately spherical in shape. The majority of the nanocrystallite's size is approximately 30 nm. This is consistent with the X-ray diffraction result.

Results indicate that separately using $CeCl_3{\cdot}7H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$ and $Ce_2(SO_4)_3{\cdot}9H_2O$ in place of $Ce(Ac)_3{\cdot}3H_2O$ as the reactant as synthesized according to the conditions of No.1 to 4 in TABLE 2, yield similar XRD patterns, TEM results and the ED patterns as when using the latter. All these experiments resulted in the synthesis of single nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium). The X-ray diffraction analysis results are indicated in TABLE 1. But it can be seen from the TEM graph that the particle for nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) of different reactants are eavenly dispersed and the order of granular sizes is: $Ce(Ac)_3{\cdot}3H_2O<Ce(NO_3)_3{\cdot}6H_2O<$

TABLE 1 : X-ray diffraction result of the $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) nanocrystallites

Reaction system	the liquid phase synthesis $Ce_2(C_4H_4O_6)_3$	Reaction system	$Ce(Ac)_3{\cdot}3H_2O + C_4H_4O_6 \rightarrow Ce_2(C_4H_4O_6)_3$
$2\theta/(^0)$	12.7 19.6 29.5 40.8 52.3 62.7	$2\theta/(^0)$	12.6 19.5 28.9 41.2 52.3 61.9
d/Å	1.6 2.3 10.7 12.3 13.1 12.6	d/Å	1.5 2.2 10.6 12.5 13.2 12.9
Reaction system	$CeCl_3{\cdot}7H_2O + C_4H_4O_6 \rightarrow Ce_2(C_4H_4O_6)_3$	Reaction system	$Ce(NO_3)_3{\cdot}6H_2O + C_4H_4O_6 \rightarrow Ce_2(C_4H_4O_6)_3$
$2\theta/(^0)$	12.8 19.7 29.6 41.1 52.7 62.7	$2\theta/(^0)$	12.9 19.2 29.3 40.6 52.1 62.2
d/Å	1.7 2.5 10.8 12.5 13.2 12.8	d/Å	1.6 2.2 10.5 12.7 13.2 12.8
Reaction system	$Ce_2(SO_4)_3{\cdot}9H_2O + C_4H_4O_6 \rightarrow Ce_2(C_4H_4O_6)_3$	Reaction system	the purity with analyses $Ce_2(C_4H_4O_6)_3$
$2\theta/(^0)$	12.6 19.8 29.2 40.6 52.1 61.9	$2\theta/(^0)$	12.7 18.9 29.2 41.2 52.1 62.3

d/Å	1.6 2.3 10.7 12.3 13.1 11.9	d/Å	1.8 2.2 10.9 12.6 13.2 12.8

TABLE 2 : Morphology and particle size of the $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) nanocrystallites under different reaction conditions by solid-state reaction

No.	Mole ratio	Inert substance and ratio of mixture (between Ce)	Solvent (1 mL)	Reaction time/min	Morphology	Particle size/nm	Yield /%
1	$Ce(Ac)_3·3H_2O$, $C_4H_4O_6$ (1:3) :1.5)(1:3)			30	Approx ball shape	60	90.2
2	$Ce(NO_3)_3·6H_2O$, $C_4H_4O_6$ (1:3)			30	Approx ball shape	70	90.1
3	$Ce_2(SO_4)_3·9H_2O$, $C_4H_4O_6$ (1:3)			30	Approx ball shape	80	89.0
4	$CeCl_3·3H_2O$, $C_4H_4O_6$ (1:3)			30	Approx ball shape	90	87.9
5	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:6)			30	Approx ball shape	50	86.2
6	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:9)			30	Approx ball shape	50	83.1
7	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaCl (8:1)		30	Approx ball shape	50	87.3
8	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(1:1)		30	Approx ball shape	50	85.1
9	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(2:1)		30	Approx ball shape	40	87.8
10	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(4:1)		30	Approx ball shape	40	89.2
11	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)		30	Approx ball shape	50	82.6
12	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(16:1)		30	Approx ball shape	50	81.3
13	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(32:1)		30	Approx ball shape	50	81.7
14	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)	Alcohol	30	Approx ball shape	60	81.2
15	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)	Acetonitrile	20	Approx ball shape	50	81.5
16	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)	Acetonitrile	30	Approx ball shape	30	87.6
17	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)	Acetonitrile	60	Rhombus shape	40	81.2
18	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)	Phenthiol	30	Rhombus shape	60	81.7
19	$Ce(Ac)_3·7H_2O$, $C_4H_4O_6$ (1:3)	NaAc(8:1)	OP*	30	Approx ball shape	70	82.3

OP*: poly ethylene glycol dioctyl ether

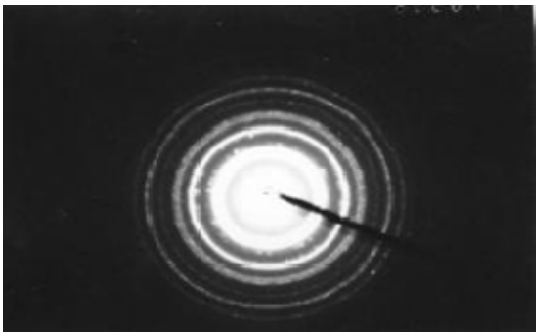

Figure 1 : The ED pattern of the $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) nanocrystallites (synthesized according to No.16 in TABLE 2)

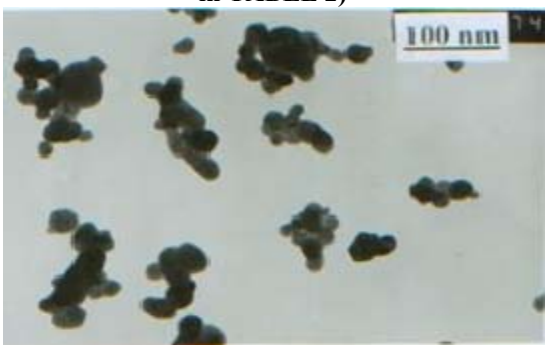

Figure 2 : TEM photograph of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) nanocrystallites (synthesized according to No.16 in TABLE 2)

$Ce_2(SO_4)_3 \cdot 9H_2O$<$CeCl_3 \cdot 7H_2O$ (TABLE 2), among which the particle size of nanocrystallite $Ce(Ac)_3 \cdot 3H_2O$ is the smallest. During experimentation, observing from changing rate of the mixture's color after reactants are mixed and porphyrized indicates the speeds of reaction are different. Using $Ce(Ac)_3 \cdot 3H_2O$ as the reactant, yielded the fastest rate of reaction and the faster the reaction speed is, the faster the speed of nucleation growth. With the growing speed of nucleus remaining constant. Therefore the granular size of the synthesized with $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is smaller.

Results indicate that by adding inert substances like NaCl and NaAc can produce smaller particle sizes, X-ray powder diffraction (XRD) of the products with the latter yielding results slightly better. X-ray powder diffraction (XRD) results of different matching proportions (synthesized according to No.7 to 13 in TABLE 2) shows that the XRD pattern of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is similar to the standard XRD pattern of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium), and that the product is a nanocrystalite. It can be seen from the TEM photograph that the particle of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is in the shape of a rhombus. Moreover, the larger the matching proportion of NaAc is, the smaller the produced particle size of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) becomes. When the matching proportion reaches 16:1, the size of t he particle diameter will be about 50 nm.

In solid-state reaction those substances that do not take part in the reaction all belong to inert substances, and the appropriate amount of inert substances, the ones which can be added in order to change the speed of nucleation and the nucleus's growth. On one hand, the added insert substances can make the reactant be more dispersive and mix more evenly, and make the growing speed of the product particle slow down and the produced particle becomes less. On the other hand, by adding insert, the reaction speed of th e system and the speed of nucleation would slow down. Therefore, the matching proportion should be appropriately controlled so as to achieve the best result.

The XRD pattern of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) synthesized by adding various kinds of trace solvents or surfactants (synthesized according to No.14 to 19 in TABLE 2) all yielded similar results as well. All the products from these reactions were single phase nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium). It can be seen from the TEM graph that by adding trace solvent or surfactant, the

product particle size becomes slightly smaller and the particle diameters are more evenly dispersed. Solvents or surfactants can promote the contact and dispersion of the reactants in solid-state reaction system, and quicken the reaction speed. Among the solvents and surfactants tested the best result yielded acetonitrile.

Different time spent on porphyrizing the reactant, the XRD pattern of $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) are similar. However, the size differences of the $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) nanocrystallite particles are minimal between a porphyrization time of 20 min and 30 min. However, after porphyrizing the reactants for 60 min, the nanocrystallite particle sizes becomes larger (synthesized according to No.15, 16, 17 in TABLE 2). After 30 min of porphyrizing, the chemical reactions is basically complete and if porphyrization continues, the growth of the nanocrystalline nucleus becomes the main reaction process. Therefore, resulting in a larger diameter of the nanocrystalline particle. The TABLE 2 shows the TEM graph of the nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) (synthesized according to No.17 in TABLE 2). The graph indicates that the produced nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is rhombus spherical, most of which are about 40 nm in size.

CONCLUSIONS

In conclusion, under near ambient temperature and ultrasonication, nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) can be synthesized by solid-state reaction. The resulting particle sizes are relatively uniform, the morphology of the crystal is spherical, and the average particle diameter is about 30 nm.

Furthermore, during the synthesis of nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium), varying the solid-state reaction conditions such as the types of reactants, matching proportion of reactants, additions of inert substance, addition of trace solvents or surfactants and porphyrization time may influence the morphology, particle size and size distribution of the final products. The best condition for solid-state synthesis nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) involves the utilization of $Ce(Ac)_3{\cdot}3H_2O$ and $C_4H_4O_6$ (1:3) as reactants, addition of inert substance at a ratio of 8 to 1 acetonitrile (1 mL). The synthesis is achieved during a porphyrization period of 30 min under heatred conditions. Finally, the yield rate of nanocrystalline $Ce_2(C_4H_4O_6)_3$ (tartaric acid cerium) is approximately 87.6%.

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