

Hierarchical strontium carbonate submicron spheres self-assembled under hydrothermal conditions

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Uniform hierarchical strontium carbonate (SrCO_3) submicron spheres bearing detectable cavities on the surfaces and porous structures within the body were efficiently obtained, by a facile hydrothermal treatment (190 °C, 12 h) of the room temperature precipitate derived from Na_2CO_3 and SrCl_2 solution. MgCl_2 and ethylene diamine tetraacetic acid (EDTA) disodium salt were used as the additives. The as-obtained submicron spheres were self-assembled by crystalline SrCO_3 nanoparticles under hydrothermal conditions. The present hydrothermally synthesized hierarchical SrCO_3 submicron spheres would enlarge the potentials of SrCO_3 micro-/nanostructures in the hierarchical architectures and porous materials family for further applications in the fields of catalysis, composites, adsorbents, and devices, etc.

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1 Introduction

Complex architectures, especially three-dimensional hierarchical architectures have attracted extraordinary attention and intensive interests due to their unique structures and fantastic properties different from those of the monomorph structures [1]. The hierarchical structures are expected to play a significant role in fabricating the high performance nanocomposites [2], energy conversion and storage device [3], efficient catalyst [4], and adsorbent for water treatment [5].

Recently, three-dimensional hierarchical architectures of strontium carbonate (SrCO_3), such as flowerlike [6,7], bundle-like, dumbbell-like, hexagonal star-like [8,9], branch-like [10], especially spherical or sphere-like [7-9,11,12] SrCO_3 microstructures, have attracted extraordinary attention due to their novel applications as chemiluminescence sensors [13], catalyst [14,15], etc., in addition to their traditional utilizations as additives in the production of iridescent and specialty glasses for color television tubes, strontium metal and other strontium compounds [16,17]. SrCO_3 microspheres bearing smooth surfaces could be formed by enzyme-catalyzed decomposition [11], room temperature aging method in presence of appropriate additives, such as poly-(styrene-alt-maleic acid) (PSMA) [8] and ethylene diamine tetraacetic acid (EDTA) [9], and also microemulsion-mediated solvothermal synthesis in presence of cetyltrimethylammonium bromide (CTAB) [12]. Very recently, mesoporous SrCO_3 spheres derived from room temperature ionic liquid (ILs) [18] and hierarchical SrCO_3 architectures originated from room temperature aging method (5 days) based on the conversion of pre-synthesized SrCrO_4 nanowires [19] have also been reported. In contrast, facile synthesis of SrCO_3 submicron spheres in aqueous solution within a short time is still an open question.

On the other hand, as one of the most efficient methods of soft chemistry, hydrothermal technologies have been widely employed in the process of one-dimensional (1D) nanostructures [20-22] because of the distinct advantages over other traditional methods [23]. Most recently, hydrothermal method has also been emerged as a thriving technique for the facile fabrication of the complex hierarchical architectures, such as cantaloupe-like AlOOH superstructures [24], hierarchical $\text{Ni}(\text{OH})_2/\text{NiO}$ hollow architectures [25], hierarchical Bi_2WO_6 microspheres [26] and octahedron-like structures [27], monodispersed colloidal carbon spheres [28], and hierarchical InVO_4 mesoporous microspheres [29]. In this contribution, we report a facile hydrothermal

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strategy for hierarchical SrCO₃ submicron spheres with detectable cavities on the surfaces and porous structures within the body, which are self-assembled by related nanoparticles under hydrothermal conditions in presence of EDTA disodium salt and MgCl₂ as additives.

2 Experimental

Synthesis SrCO₃ submicron spheres were synthesized via a room temperature coprecipitation of SrCl₂ and Na₂CO₃ followed by a facile hydrothermal treatment, in presence of appropriate amount of MgCl₂ and EDTA disodium salt as additives. In a typical procedure, Na₂CO₃ (1.41 mol·L⁻¹, 10 mL) was dropped into SrCl₂ (1.41 mol·L⁻¹, 11 mL) under vigorous magnetic stirring at room temperature (dropping rate: 1 droplet per sec approx), leading to a white slurry. EDTA disodium salt (0.4187 g) and MgCl₂·6H₂O (0.1398 g) were added into the previously resultant and continuously stirred slurry, keeping molar ratios of EDTA disodium salt as well as MgCl₂ to Na₂CO₃ as 5%. The slurry was supplied deionized (DI) water to 55 mL and kept stirring for another 3 min., and then transferred into a Teflon-lined stainless steel autoclave with a capacity of 70 mL. The autoclave was sealed and heated (1 K min⁻¹) to 190 °C and kept in an isothermal state for 12 h and then cooled down to room temperature naturally. The precipitate was filtered, washed with DI water and absolute alcohol for three times, respectively, and finally dried (120 °C, 6 h) for further characterization.

Characterization Crystal phase and structure of the sample were identified by the X-ray powder diffractometer (XRD, D/MAX 2500, Rigaku, Japan) using a Cu K_α radiation. Morphology, microstructure and composition of the samples were examined by the field emission scanning electron microscopy (SEM, JSM 7401F, JEOL, Japan) operated at 3.0 kV, and a high resolution transmission electron microscopy (TEM, JEM-2010, JEOL, Japan) performed at 120.0 kV equipped with an X-ray energy dispersive spectrometer (EDS, INCA Energy TEM, Oxford Instruments, UK) and a charge coupled device (CCD) camera (Orius SC 1000, Gatan, USA). For TEM and EDS analyses, the sample was first dispersed in ethanol by ultrasonic treatment for 15 min and then deposited onto the holey carbon film supported by a copper grid. The thermal decomposition behavior of the sample was detected by the thermo-gravimetric analyzer (TGA, Netzsch STA 409C, Germany) carried out in dynamic air with a heating rate of 10.0 K min⁻¹. Size distribution of the submicron spheres was estimated by direct measuring about 200 particles from the typical SEM images. Ultraviolet-visible (UV-vis) absorption spectra were recorded by a Varian Cary-300 spectrophotometer.

3 Results and discussion

XRD patterns, SEM images and size distribution of the hydrothermal product (190 °C, 12 h) in absence or presence of additives are shown in figure 1. Hydrothermal treatment of the slurry containing the room temperature coprecipitation in absence of additives led to polyhedron-like orthorhombic SrCO₃ (Fig. 1a₁) particles with well-defined facets and distinct wide size distribution (Fig. 1b). In contrast, hydrothermal treatment of the same slurry in presence of additives (EDTA disodium salt and MgCl₂) resulted in orthorhombic SrCO₃ (Fig. 1a₂) submicron spheres with a uniform hierarchical structure bearing detectable cavities on the surfaces (Fig. 1c,c₁) and also a narrow size distribution (Fig. 1d). It can be seen that, whether the additives are present or not, all diffraction peaks of the XRD patterns (Fig. 1a₁₋₂) could be readily indexed to the orthorhombic phase of SrCO₃ (strontianite, PDF# 05-0418). The distinct difference between the diffraction intensity of the XRD patterns might be attributed to the differences of the morphology especially the average size of the hydrothermal product. The remarkable broadening of the diffraction peaks of the XRD pattern (Fig. 1a₂) revealed the existence of crystalline SrCO₃ nanoparticles within the submicron spherical structure, in accordance with the SEM observation (Fig. 1c,c₁). Meanwhile, the crystallite size along the [111] direction (D_{111}) calculated by the Debye-Scherrer equation was 14.5 nm. Thus, the hydrothermal treatment of the room temperature precipitate in presence of appropriate EDTA disodium salt and MgCl₂ as additives didn't alter the chemical composition whereas greatly influenced the morphology of the hydrothermal product. The specific morphology of the present hierarchical SrCO₃ submicron spheres was somewhat like the spherical SrCO₃ with smooth surface reported in the literature by other methods [8,9,11,12], and quite similar to the mesoporous SrCO₃ spheres obtained in room temperature ILs [18]. Meanwhile, the statistical data (Fig.1d) demonstrated that, approx 95% of the hierarchical SrCO₃ submicron spheres had a diameter within the range of 600 nm to 1100 nm, indicating a narrower diameter distribution compared with that of the mesoporous SrCO₃ spheres

obtained in ILs containing two types of spheres with a diameter of 300–400 nm and 60–100 nm [18].

Formation of the hierarchical SrCO_3 submicron spheres could be expressed in ionic form as follows:

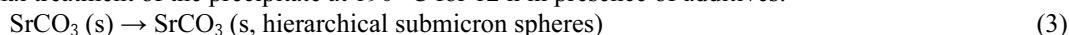
Room temperature coprecipitation of Na_2CO_3 and SrCl_2 :



Hydrothermal treatment of the precipitate at 190 °C for 12 h in absence of additives:



Hydrothermal treatment of the precipitate at 190 °C for 12 h in presence of additives:



It was worth noting that, Na^+ (a.q.) as well as Cl^- (a.q.) was remained in the reactant system during the room temperature coprecipitation and subsequent hydrothermal treatment, and finally removed by post treatment such as filtration and washing after the hydrothermal treatment. On the other hand, to avoid the introduction of unwanted impurity MgCO_3 by the possible side reaction between Na_2CO_3 and MgCl_2 , Na_2CO_3 was dropped into SrCl_2 solution, and the amount of SrCl_2 was strictly kept relatively excessive corresponding to that of Na_2CO_3 , in particular, the additives were added into the system after the accomplishment of Na_2CO_3 feeding. Thus, Mg^{2+} was also remained within the reaction system during the hydrothermal treatment and ultimately removed by subsequent filtration and washing.

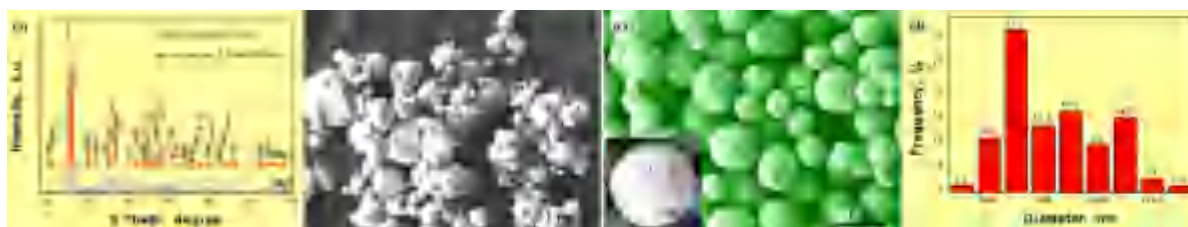


Fig. 1 XRD patterns (a), SEM images (b–c) and size distribution (d) of the hydrothermal product obtained in absence (a₁, b) or presence (a₂, c, c₁, d) of EDTA disodium salt and MgCl_2 as additives (molar ratio, additives: Na_2CO_3 =5:100, SrCl_2 : Na_2CO_3 =1.1:1, 190 °C, 12.0 h). Inserted figure (c₁) shows a high resolution SEM image of the SrCO_3 submicron spheres. (Online color at www.crt-journal.org)

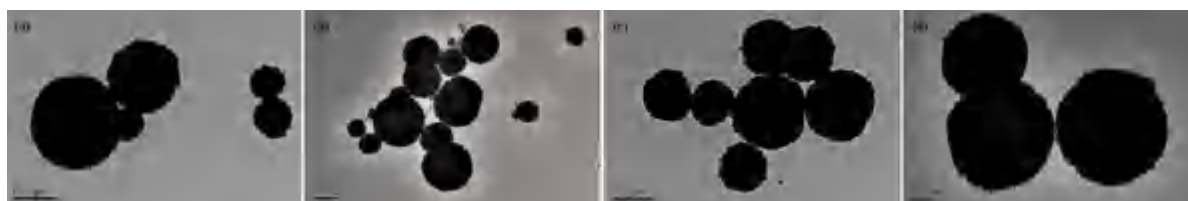


Fig. 2 Effects of the molar ratio of SrCl_2 : Na_2CO_3 on the morphology and size distribution of the hydrothermally synthesized submicron SrCO_3 spheres. Temperature (°C): 190; Time (h): 12.0; EDTA disodium salt: Na_2CO_3 =5:100; MgCl_2 : Na_2CO_3 =5:100; SrCl_2 : Na_2CO_3 =1.02:1 (a), 1.05:1 (b), 1.2:1 (c), 1.1:1 (d).

Molar ratio of the reactants, i.e. SrCl_2 : Na_2CO_3 , has significant effect on the morphology and size distribution of the hydrothermally synthesized SrCO_3 submicron spheres (190 °C, 12.0 h), as shown in figure 2. When the molar ratio of the reactants SrCl_2 : Na_2CO_3 changed within the range of 1.02:1–1.2:1 (Fig. 2a–d), 1.1:1 (Fig. 2d) was proved as the optimum molar ratio needed for the hydrothermal formation of the uniform hierarchical submicron spheres with narrow size distribution, with the molar ratio of the additive EDTA disodium salt, as well as MgCl_2 to Na_2CO_3 kept as 5:100. Meanwhile, the pH value of the solution phase was slightly dropped down from original ca. 6.2 to final ca. 5.8–5.9 during the hydrothermal treatment, revealing the weak acidic environment necessary for the formation of the uniform hierarchical SrCO_3 submicron spheres.

Figure 3 shows the TEM images, corresponding EDS spectrum and selected area electron diffraction (SAED) pattern of the hierarchical submicron SrCO_3 spheres. TEM images (Fig. 3a,c) indicated the hierarchical architectures of uniform spherical morphology. EDS spectrum (Fig. 3b) recorded from the focused section (denoted as the dashed green circle) of the spheres hanging within the hole of the holey carbon film (Fig. 3a) definitely indicated that the submicron spheres comprised Sr, C and O, taking into consideration the background element Cu derived from the employed copper grid. A small submicron sphere (diameter: ca. 200 nm) was particularly selected for a closer observation with a higher magnification, so as to be feasible for

the SAED performance. The high magnification TEM image (Fig. 3c) clearly showed that the selected small submicron sphere was aggregated by multitudinal nanoparticles (diameter: 20–40 nm), and the assembly even left some detective pores with a diameter of ca. 10 nm not only on or near the surface but also within the inner of the sphere. Meanwhile, the corresponding SAED pattern (Fig. 3d) exerted some regularly aligned bright spots and also blur diffraction rings, indicating the crystalline phase of the nanoparticles within the submicron spheres, and the blur diffraction rings containing relatively bright spots could be indexed as the planes of (111), (200), (221), (222) and (151), which were thus in agreement with the previous XRD results (Fig. 1a₂). Although the submicron spheres looked like the agglomeration of SrCO₃ nanoparticles (in other words, loosely attached nanoparticles), the uniform hierarchical SrCO₃ submicron spheres were believed to be self-assembled by the related crystalline nanoparticles in presence of appropriate additives, rather than the random agglomeration.

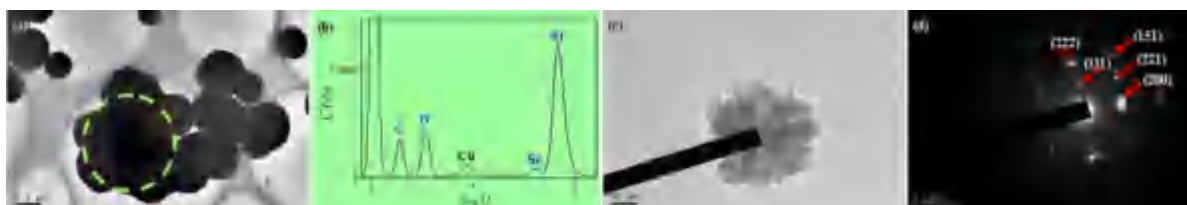


Fig. 3 TEM images (a, c), EDS spectrum (b) and SAED pattern (d) of the hydrothermally synthesized SrCO₃ submicron spheres deposited onto the holey carbon film (a, b) or ordinary carbon film (c, d) supported by a copper grid (molar ratio, additives: Na₂CO₃=5:100, SrCl₂:Na₂CO₃=1.1:1, 190 °C, 12.0 h). (Online color at www.crt-journal.org)



Fig. 4 Higher magnification TEM images (a, b) and HRTEM image (c) of the hydrothermally synthesized SrCO₃ submicron spheres deposited onto the holey carbon film, supported by a copper grid (molar ratio, additives: Na₂CO₃=5:100, SrCl₂:Na₂CO₃=1.1:1, 190 °C, 12.0 h).

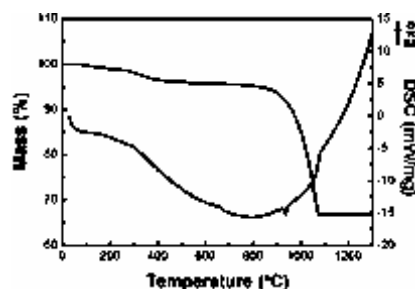
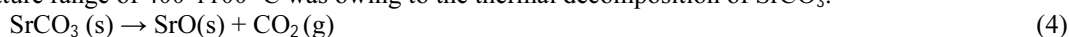


Fig. 5 TG-DSC curves of the hydrothermally synthesized SrCO₃ submicron spheres (molar ratio, additives: Na₂CO₃=5:100, SrCl₂:Na₂CO₃=1.1:1, 190 °C, 12.0 h).

Evolution behavior of the nanoparticles attached to the SrCO₃ submicron spheres under the irradiation of the electron beam was recorded, as shown by the red dotted-line rectangular region in figure 4. Several nanoparticles assembled into a cross-hands profile were selected and then focused with the electron beam (Fig. 4a). With the irradiation time went on, the focused nanoparticles gradually bent over, further inclined to the surface, and finally embedded into the submicron sphere (Fig. 4b), definitely indicating the porous structure existed within the submicron spheres. As a matter of fact, SEM (Fig. 1c,c₁) and TEM (Fig. 3c, Fig. 4a) images also confirmed the porous structures within the submicron spheres, which prefigured the potential applications of the present SrCO₃ submicron spheres as the support of the catalyst and also the adsorbents for the pigment-containing effluent treatment. Meanwhile, within the red dotted-line rectangular region of the submicron sphere surface (Fig. 4b), there interplanar spacings of 0.337 nm detected from the legible lattice fringes (Fig. 4c), quite similar to that of the (021) planes for the stand orthorhombic SrCO₃. After irradiated by the electron beam for some long time, the submicron sphere got a relatively smooth surface. This is helpful for understanding the hydrothermal effect on the formation of the hierarchical SrCO₃ submicron spheres, which created an environment of high temperature and high pressure and thus facile for the transportation of the building blocks.

Figure 5 shows the TG-DSC curves of the hydrothermally synthesized SrCO₃ submicron spheres. The mass of the samples decreased from 99.95% (30 °C) to 98.19% (300 °C) to 96.58% (400 °C), then to 93.67 (900 °C),

finally to 66.77% (1100 °C) and kept constant thereafter. The mass loss of 3.38% before the temperature as 400 °C might be attributed to the loss of the adsorbed water, and the subsequent mass loss of 29.81% between the temperature range of 400–1100 °C was owing to the thermal decomposition of SrCO₃:



The corresponding mass loss was quite similar to the theoretical value of the mass loss of the above decomposition (29.81%), and almost the same with that occurred for the thermal decomposition of the high pure SrCO₃ phase between 900–1150 °C [30]. The relatively low decomposition temperature of the present SrCO₃ submicron spheres might be ascribed to the size effect of the nanoparticles existed within the submicron spheres. Meanwhile, the DSC curve indicates that there existed a broad endothermic vale within the whole temperature range of the heating procedure especially between 400–1100 °C, which also contains a remarkable endothermic peak at the temperature of 935.3 °C related to the conversion from the orthorhombic α -SrCO₃ phase to the trigonal β -SrCO₃ phase [30].

The UV-vis absorption spectra (not shown here) recorded from the uniform hierarchical SrCO₃ submicron spheres demonstrated that, the spectra was entirely featureless and there existed no obvious absorption edge in the wavelength range of 200–350 nm, indicating that the uniform hierarchical SrCO₃ submicron spheres were transparent within the ultraviolet region [31].

The nanocrystals existing within the submicron spheres, revealed by the XRD pattern (Fig. 1a₂), the small spherical aggregates (Fig. 3c) and also the quasi polycrystalline characteristic SAED pattern (Fig. 3d), prefigured the probable assembling behavior of the related nanoparticles in course of the hydrothermal formation of the uniform hierarchical SrCO₃ submicron spheres in presence of additives. In addition, for our case, EDTA disodium salt and MgCl₂ were both required for the hydrothermal formation of the present hierarchical SrCO₃ submicron spheres, and the specific assembly mechanism for the nanoparticles into the uniform hierarchical submicron spheres in presence of the additives was still under investigation. Besides, compared with literature results, the present SrCO₃ submicron spheres containing porous structures are distinctly different with the previously reported smooth-surface SrCO₃ spheres [8,9,11,12] and also those SrCO₃ architectures of other morphologies [6–10], thus suggested new potential applications of SrCO₃ in the fields such as catalysts, composites, adsorbents, and devices. Moreover, the employed hydrothermal synthesis does not need much organic solvents or ILs, thus is an efficient promising and alternative green synthetic route to the hierarchical SrCO₃ architectures, which can also be extended to the preparation of other carbonates with similar structures.

4 Conclusion

In summary, uniform hierarchical SrCO₃ submicron spheres bearing detective cavities on the surfaces and porous structures within the body, with a diameter within the range of 600 to 1100 nm and a narrow diameter distribution, were efficiently obtained by a facile hydrothermal treatment (190 °C, 12 h) of the room temperature precipitate derived from Na₂CO₃ and SrCl₂ solution in presence of appropriate amount of MgCl₂ and EDTA disodium salt as additives. The present uniform hierarchical SrCO₃ submicron spheres were self-assembled by the related crystalline nanoparticles under hydrothermal conditions, assisted by the additives, and the novel hierarchical structures would enlarge the potential applications of SrCO₃ micro/nanostructures in the hierarchical architectures and porous materials family as catalysts, composites, adsorbents, and devices, etc. Moreover, the developed facile hydrothermal strategy may also be expected for the preparation of other carbonates with similar hierarchical porous structures.

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