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A general process to synthesize self-assembled shell-like $(Ca_{0.61}, Nd_{0.26})TiO_3$ clusters

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ABSTRACT

Homogenous $(Ca_{0.61}, Nd_{0.26})TiO_3$ self-assembled shell-like clusters with serrated surface were synthesized by sol–gel method with one step. As the dried gel was heat-treated at 800 °C for 100 min with rising temperature, the shell-like clusters with perovskite structure were obtained, which were induced by the heat and polyacrylate. The size of shell-like clusters is about 2.5 μm. Selected area electron diffraction analysis demonstrated that the particles was polycrystalline. Possible reaction process in sol–gel and possible formation mechanism of the shell-like clusters were discussed.

1. Introduction

Materials with new and enhanced properties can be obtained by combining, at a molecular level, inorganic and organic building blocks [1,2]. Hydrolysis and condensation reactions leaded to the formation of macromolecular networks, providing the unique possibility of tailoring the precursor compounds according to the desired process path. Transition metal oxoclusters and perovskite structure based hybrid materials clusters were synthesized by some groups because of their novel structure and special application [3,4]. The methacrylate modified barium–titanium and barium-based oxoclusters were synthesized for the development of methacrylate-based inorganic–organic hybrid materials [3]. Dual shell-like framework structures featuring an outer shell of Ni ions encapsulating a smaller and inner shell of Ln ions have also been obtained for three discrete cluster complexes [5] and binary transition metal clusters were synthesized [6]. Other metal clusters have also been newly investigated, such as Al_n clusters, and the relative theoretical studies have been carried out to study the ground-state structures [7–9]. Some results generally found that desirable controllable synthesize of clusters could be obtained by using different ligands sizes [10,11]. Although the clusters of synthesis have enjoyed great development in recent years, special attention has been paid to inorganic shells because of their relatively high thermal, mechanical and chemical stability. Thus, various oxides and sulfides have been prepared in the form of microcapsules, namely, with spherical geometry [12,13].

$CaTiO_3$ as an important dielectric material has attracted much attention because of its high dielectric constant. However, compared with other complex perovskite structure materials, the dielectric loss of $CaTiO_3$ was rather high [14]. In order to solve the problem, several groups attempted to substitute Ca^{2+} by lanthanide (trivalent ions as La^{3+}, Sm^{3+}, and Nd^{3+}) ions in $CaTiO_3$ structure [15–17]. Yoshida had systematically researched the $(Ca_{1-x}, Nd_{2x/3})TiO_3$ system with different x value via solid-state method and found that $(Ca_{0.61}, Nd_{0.26})TiO_3$ had the highest dielectric constant and the lowest dielectric loss [17]. In previous work of our group, we synthesized $(Ca_{0.61}, Nd_{0.26})TiO_3$ nanoparticles at a relatively low temperature and the dielectric loss of the ceramics synthesized by the particles decreased further by sol–gel method. $(Ca_{0.61}, Nd_{0.26})TiO_3$ ceramics materials would be promising materials for tunable microwave applications because of its high dielectric constant (ε) and relatively low losses [18] and the dielectric properties and the applications are very sensitive to morphology of the system [19–21].

In recent years there has been an increasing interest in the fabrication of colloidal shell-like aggregation clusters [22–24]. The modification of fine particles by coating with inorganic materials of different composition or binary inorganic phase has been extensively studied to change their interfacial characteristics [25] as well as their optical, magnetic, catalytic, and thermal properties [26–28]. However, the perovskite structure based shell-like clusters without any organic materials absorbed has not been fully explored yet. In this study, we found that $(Ca_{0.61}, Nd_{0.26})TiO_3$ perovskite structure shell-like cluster particles were obtained by sol–gel method.

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2. Experimental

2.1. Synthesis of the $(Ca_{0.61}, Nd_{0.26})TiO_3$ shell-like clusters

The core-shell inorganic particles were synthesized according to traditional sol–gel method. Neodynium nitrate hexahydrate [$Nd(NO_3)_3{\cdot}6H_2O$, 99.9%], calcium nitrate tetrahydrate [$Ca(NO_3)_2{\cdot}4H_2O$, 99.9%] and tetrabutyl titanium [$Ti(C_4H_9O)_4$, 99%] were used as raw materials. Ammonium polyarylate which was purchased from Alfa Aesar was used as surfactant. 34.32 g (0.1 mol) of $Ti(C_4H_9O)_4$ was added to 111 ml ethanol with constant stirring using a magnetic stirrer for 1 h. The $Nd(NO_3)_3{\cdot}6H_2O$ (11.40 g) and $Ca(NO_3)_2{\cdot}4H_2O$ (14.39 g) were dissolved into 29 ml and 77 ml ethanol, respectively. The $Nd(NO_3)_3{\cdot}6H_2O$ and $Ca(NO_3)_2{\cdot}4H_2O$ ethanol solution were then added to the $Ti(C_4H_9O)_4$ solution drop-by-drop. Nitrate acid ethanol solution was used to adjust the pH value to about 2.5. Ammonium polyacrylate (0.75 wt%, of the total particles weight) was diluted in 5 ml ethanol and then dropped into the hybrid solution, accompanied with the light purple transparent solution turned into light purple translucent solution. The Nd^{3+} ions, Ca^{2+} ions and polyacrylate anions were distributed homogeneously in the solution and the sol with precursor concentration of 0.9 mol/L was formed with 100 min vigorous stirring. Then the sol was aged for 24 h in a thermostatic bath at 28 °C until it turned into elastic gel completely. The gel was dried at 80 °C for about 30 h, and then the dried gel was heat-treated at 500–800 °C for 100 min with rising temperature and cooled at room temperature.

2.2. Measurements

The phase composition of the particles was investigated by X-ray powder diffraction (RIGAKUD/max 2550 PC, Rigaku Co., Tokyo, Japan) using Cu Kα radiation. The XRD datum were collected over the range of $2\theta = 10$–80° with a step size of 0.02°. Transmission electron microscopy (TEM, JEM-1230EX) was employed to characterize the structure and measure the particle size, and selected area electron diffraction (SAED) analysis was operated. The surface morphology of the particles was characterized by scanning electron microscopy (SEM, JEOL-JSM-5610LV). The EDS analysis was performed using an Oxford instrument eXL EDS system. Transform infrared (FT-IR) spectra measurements were carried out by means of Nicolet 400 spectrometer in the 4000–400 cm^{-1} wavenumber range using KBr pellets.

3. Results

X-ray diffraction patterns of the clusters are shown in Fig. 1. The major phase of $(Ca_{0.61}, Nd_{0.26})TiO_3$ with orthorhombic perovskite structure has no obvious change, but the minor phase of $CaCO_3$ becomes less gradually with the addition quantities of the ammonium polyacrylate increased. However, the $CaCO_3$ phase is nearly disappeared but little TiO_2 phase is appeared, when the quantum addition of ammonium polyacrylate is increased to 0.75 wt%. Fig. 2 shows the XRD patterns of the gel heat-treated from 500 °C to 800 °C for 1 h. There is no clear refraction peaks in Fig. 2(a), which indicates that the particles are completely non-crystal phase. The $(Ca_{0.61}, Nd_{0.26})TiO_3$ phase does not change any more after 600 °C, indicating that the crystal phase transition has completed. The $CaCO_3$ phase disappears gradually and little TiO_2 phase presents at 800 °C with the heat treatment temperature increased.

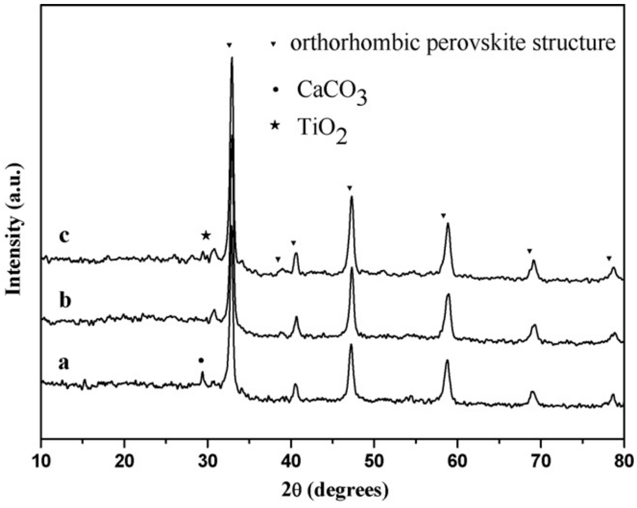

Fig. 1. X-ray diffraction patterns of the powder from the xerogel heat-treated for 100 min at 800 °C with different addition qualities of ammonium polyacrylate: (a) 0.25 wt%; (b) 0.5 wt%; (c) 0.75 wt%.

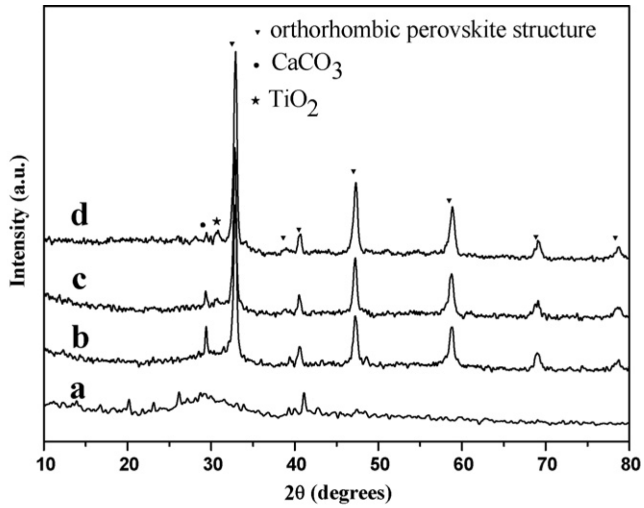

Fig. 2. X-ray diffraction patterns of the xerogel with ammonium polyacrylate addition 0.75 wt% at different heat-treated temperature for 100 min: (a) 500 °C; (b) 600 °C; (c) 700 °C; (d) 800 °C.

TEM images are shown in Fig. 3. Although the particles with a size of about 10 nm were obtained, the particles did not crystallize completely at 500 °C. The particles size increase with the temperature increasing. However, the shell-like clusters with the particle size about 2.5 μm are gained when the heat-treated temperature is up to 800 °C. The shell-like clusters are shown with serrated shells and large closed inner cavities in Fig. 3(d) at low magnification and in Fig. 3(e) at a relative high magnification. Selected area electron diffraction (SAED) analysis of the clusters exhibits diffraction rings which demonstrates that particles were polycrystalline. Scanning electron microscope (SEM) images of $(Ca_{0.61}, Nd_{0.26})TiO_3$ shell-like clusters which have serrated shells are shown in Fig. 4. The surface and the inner surface of the clusters with crystals ranged orderly exhibit in Fig. 4(a). The morphology images of the selected particles with high magnification are shown in Fig. 4(b) to characterize the surface and the inner surface of the shell. The crystals conjoin each other orderly and the cone-shaped crystals on the shell surface ranged homogeneously almost with the crystals size the same. The EDS analysis on the core-shell spheres confirms that the particles compose of titanium, neodymium, calcium and oxygen elements. The results of the EDS with the atom ratio of Ca:Nd:Ti:O = 12.97:5.63:20.26:61.24 are in accordance with the results of the XRD which have no other constituents in the compound.

Fourier transform infrared spectroscopy (FT-IR) is performed to further characterize the composition and structure of the clusters. Fig. 5 shows the spectra taken from dried gel and the dried gel heat-treats at 800 °C for 100 min. All of the samples show a relatively intense broad band in the vicinity of 500–800 cm^{-1} due to the Ti–O vibration [29]. The broad band between 400 and 500 cm^{-1} can be assigned to the Nd–O vibration which is shown in Fig. 5(b). The fading multiple bands around 830 cm^{-1} because of the formation of the Ti–O–Ti bonds in Fig. 5(a) [30] and the weak band appeared in Fig. 5(b) at 876 cm^{-1} possibly due to the formation of Ti–O–Ca bonds indicate that the major phase is formed via the process of heat treatment. The characteristic band at 1049 cm^{-1} is attributed to the Ti–O–C stretching [31]. However, in Fig. 5(b) several weak bands appeared over the characteristic band demonstrate that little Ca–O–C bonds form. The peak at 1386 cm^{-1} is assigned to

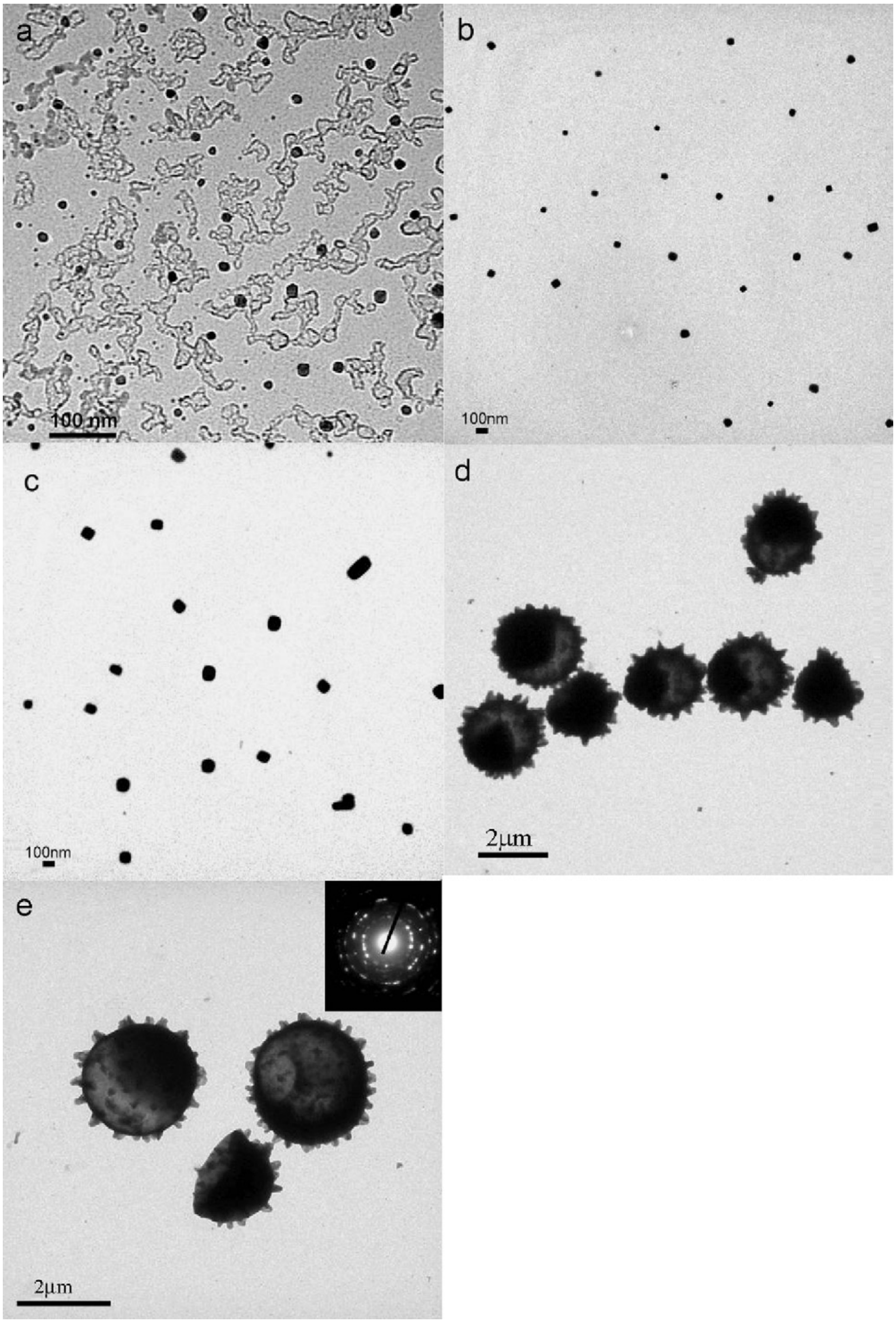

Fig. 3. TEM micrographs of the xerogel at different heat-treated temperature for 100 min: (a) 500 °C, (b) 600 °C, (c) 700 °C, (d) 800 °C with ammonium polyacrylate used as surfactant (0.75 wt%): (d) the image taken at low magnification, (e) the image taken at relative high magnification, and selected area electron diffraction (SAED) analysis of the area as shown on the top right corners of (e).

the symmetrical of CO_2^- stretching of polyacrylate anions and the peak at 1638 cm^{-1} indicates the presence of intramolecular hydrogen bonding between Ti–O–Ti and polyacrylate anions [29,32]. The broadband from 3000 to 3700 cm^{-1}, associates with the stretching vibration modes of hydroxyl groups.

4. Discussion

The sol–gel reaction is a method to prepare pure ceramic precursors at relatively low temperature. The reaction could be summarized as: hydrolysis at first to produce hydroxyl groups and then polycondensation of the hydroxyl groups and residual alkoxyl groups to form a three-dimensional network [33]. It is well known that organic additives, such as surfactants, in colloids could prevent the agglomeration of freshly formed nanoparticles during hydrolysis and calcinations treatments because the additives locate at the surface of the particles act as dispersing agents [34]. And also the pH value of the precursor solution is a decisive factor in controlling the final particle size, [35] shape, [36] phase, [37] and agglomeration, [38] due to its influence on the relative rates of hydrolysis and

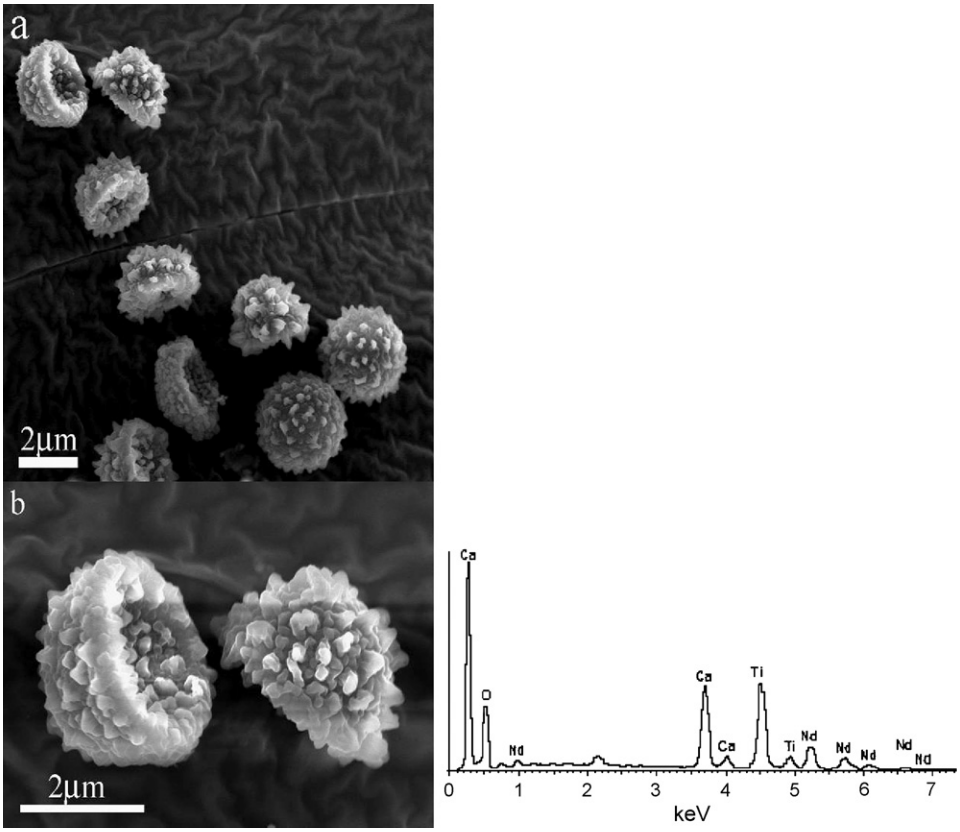

Fig. 4. SEM images of the xerogel heat-treated at 800 °C for 100 min with ammonium polyacrylate used as surfactant (0.75 wt%): (a) the image taken at low magnification; (b) the image taken at relative high magnification, and EDS analysis on the core-shell.

polycondensation. In the sol–gel system, the pH value of the system is about 2.5 and ammonium polyacrylate was used to induce the nanoparticles to self-assemble the sphere shell clusters. Many researchers find that the synthesis and stabilization of the particles of Ti system in sol–gel seem to be related to the partial hydrolysis of tetrabutyl titanium [31]. Under the experimental conditions here reported, $Ti(C_4H_9O)_4$ which reacts with polyacrylate anions and turns into less reactive species that remain bonded to Ti could be easily hydrolyzed by the addition of a nitric acid–ethanol solution. In the following stages of the process, the tetrabutyl groups may also be removed by alkoxolation.

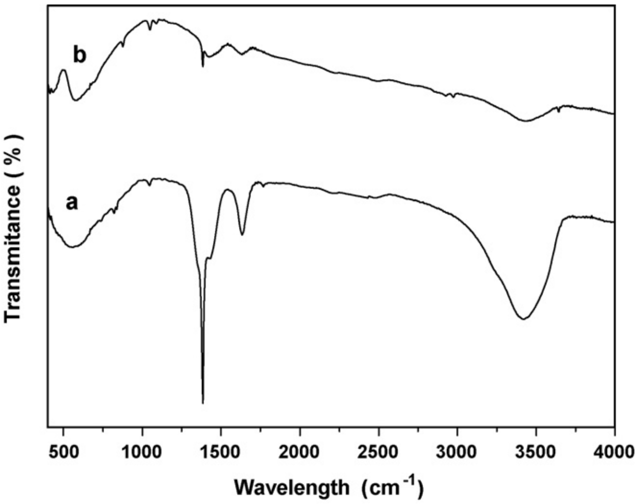

Fig. 5. FT-IR spectra of (a) dried gel of $(Ca_{0.61}, Nd_{0.26})TiO_3$; (b) the particles heat-treated at 800 °C for 100 min.

On the basis of the experimental results discussed above, we proposed a possible pathway to the hydrolysis and polycondensation process which is shown in Fig. 6. The first step leading to the condensation of the precursors involves the formation of an edge sharing dimmer between two octahedrons as shown in stage A of Fig. 6 after the $Nd(NO_3)_3{\cdot}6H_2O$ and $Ca(NO_3)_2{\cdot}4H_2O$ ethanol solution are dropped into the $Ti(C_4H_9O)_4$ ethanol solution [39,40]. During the initial stage, condensation takes place through olation reactions due to the higher liability of water with respect to –OH, $-OC_4H_9$, and monodentate and/or bidentate polyacrylate ligands. Expect H_2O, the other possible leaving groups require for acid catalysis which determines the slower rate of oxolation and alkoxolation reactions. It is the attaching of a third octahedron that determines the crystal structure, depending on whether it locates linearly or forms a twisted chain with the dimmer [41]. Stages B and C demonstrate the possible oligomerization of the embryo that proceeds through oxolation and alkoxolation because of the relative position in the dimmer of two reacting ligands, namely, $-OH_2$, –OH, OR $-OC_4H_9$, properly contributed to condensation.

The powders produced by sol–gel contain many different hydroxyls, water, and organic bonds according to the acid condition. These bonds tend to locate at the interfaces of the particles and have a large effect on nucleation and growth. In relatively high acid condition, the protonation of –OH and –O– cause more $-OH_2^+$ and $(-O-)H^+$ bonds [42] which is shown in Fig. 6. The –Ti–O–Ti– groups which have many $-OH_2^+$ and $(-O-)H^+$ bonds are extended and cause further hydrolysis. Furthermore, the –Ti–O–Ti– groups absorb polyacrylate anions to make the groups achieved electrostatic equilibrium. The long chain of the polyacrylate anions adhere to the surface of the particles which consist of –Ti–O–Ti– groups and at the same time Ca^{2+} and Nd^{3+} ions are also absorbed and dispersed into the three-dimensional networks homogeneously to

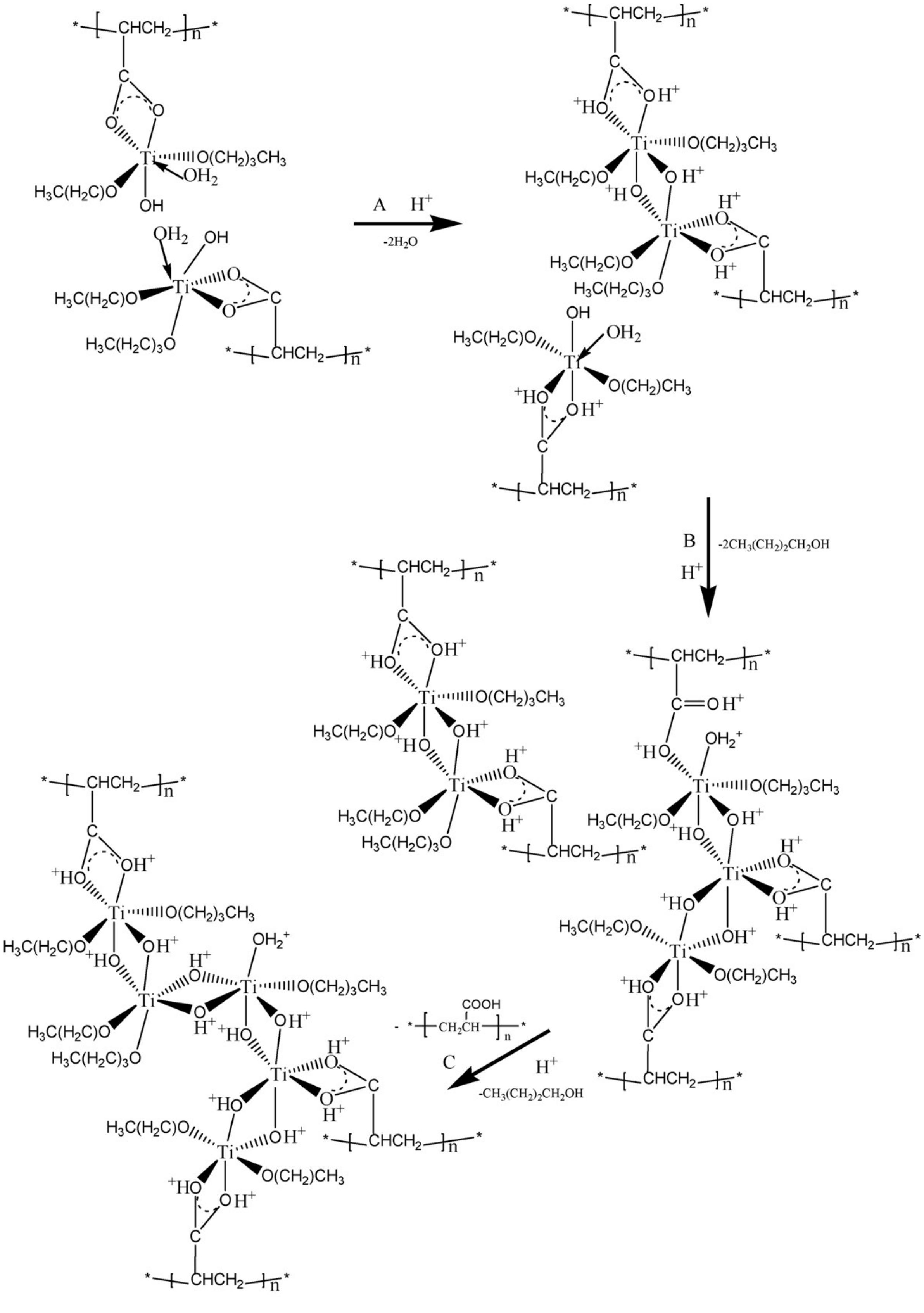

Fig. 6. Possible reaction pathway of the sol–gel system to form the initial unit cells via hydrolysis and condensation.

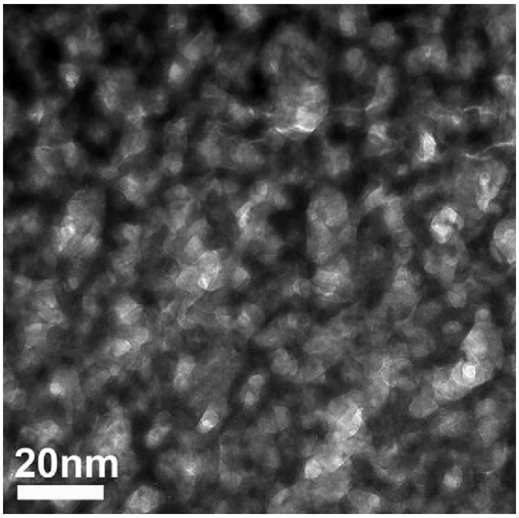

Fig. 7. The TEM images of dried gel showed the networks of the gel.

obtain kinetics and electrostatic stability of the system. The reactive –OH would make the titanate particles to form titanium hydroxyl species. Then the titanium species react with Ca^{2+} and Nd^{3+} ions to form $(Ca_{0.61}, Nd_{0.26})TiO_3$ initial unit cell [40]. Tetrabutyl titanium and water under catalysis of nitric acid hydrolyze to form the fundamental three-dimensional networks in acid condition. The TEM image in Fig. 7 shows the three-dimensional networks of the dried gel which demonstrates that in the stage of dried gel the particles remain dispersed in the inorganic–organic networks. The major phase of $(Ca_{0.61}, Nd_{0.26})TiO_3$ is obtained and the inorganic–organic networks of gel disappear. The nanoparticles with rectangular-shaped and the shell-like clusters self-assembled by the nanoparticles are gained when the gel is heat-treated at 800 °C. The nanoparticles with hydroxyl and polyacrylates absorbed on the surface self-assemble along with the activated crystal face, when the high temperature leads to hydroxyl and polyacrylate robust [43,44]. The intermolecular bands between $(Ca_{0.61}, Nd_{0.26})TiO_3$ and polyacrylate could be detected at 800 °C via FE-IR analysis, which could substantiate that the polyacrylate anions and heat induce the nanoparticles to self-assemble without template. Therefore, 800 °C is the suitable temperature which could provide appropriate energy for the self-assembly with the presence of polyacrylate.

5. Conclusions

A kind of self-assembled shell-like clusters are synthesized by sol–gel method, which consist of $(Ca_{0.61}, Nd_{0.26})TiO_3$ with regular serrated shell-like surface. The perovskite structure clusters were obtained at 800 °C for 100 min with inorganic phase only, which were induced by the heat and polyacrylate. TEM is used to characterize the clusters with the size about 2.5 μm. The selected area electron diffraction (SAED) analysis indicates that the clusters are polycrystalline. In this study, the clusters self-assemble with template-free and have good crystal spherical shells.

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