Controllable synthesis and luminescent properties of novel erythrocyte-like CaMoO₄ hierarchical nanostructures via a simple surfactant-free hydrothermal route†

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Synthesis of metal molybdates (XMoO₄, X = Ca, Sr, Ba) have received much attention recently because of their interesting structural and luminescent properties. Here novel erythrocyte-like CaMoO₄ hierarchical nanostructures are synthesized via a simple surfactant-free hydrothermal route. The formation of the calcium molybdate erythrocytes is controllable through adjusting the fundamental experimental parameters including reaction time, temperature and DMAc to H₂O ratio. The as-synthesized products are characterized using X-ray powder diffraction, scanning electron microscopy, Brunauer–Emmett–Teller and transmission electron microscopy. The results show that the nucleation and growth of the novel erythrocyte-like CaMoO₄ hierarchical nanostructures are governed by an oriented attachment growth mechanism. The luminescent properties of the CaMoO₄ erythrocytes are then studied using a spectrophotometer and the erythrocyte-like CaMoO₄ nanostructures display a strong blue emission. This study provides an easy surfactant-free synthetic route for the controllable construction of inorganic materials with high hierarchy in the absence of any surfactants.

Introduction

Self-assembled micro- and nanostructures with specific size and morphology have attracted a lot of interest in recent years owing to their significant mechanical, electrical, optical, and magnetic properties. These self-assembled hierarchical nanostructures provide promising complex functions and direct bridges between the nanoscale objects and the macroscale world. Over the past years, many self-assembled nanostructures have been synthesized using various methods. Among them, the frequently used one is the surfactant-assistant method, with which the morphology of the products could be controlled via surfactants. However, the surfactants are usually organic materials which are generally not beneficial to luminescence. Moreover, the utilization of surfactants is a complicated process that restricts the popularization of the surfactant-assisted techniques in practical applications since it will increase the production cost. Thus, it is of great significance to seek a surfactant-free method for controllable synthesis of high-quality nanostructures.

Metal molybdates (XMoO₄, X = Ca, Sr, Ba) have a great potential for application in various fields such as photoluminescence, microwave applications, optical fibers, scintillator materials, humidity sensors, and catalysis. Calcium molybdate (CaMoO₄) crystal is important amongst the metal molybdate family, which has a high potential to be applied in cryogenic scintillation detectors and double beta decays etc. Moreover, it has many interesting physical characteristics such as luminescence, reflectivity and thermal properties. Therefore, synthesis of CaMoO₄ crystals has received great attention. Crystalline CaMoO₄ microparticles were fabricated via a rapid peptide induced precipitation. CaMoO₄ flower-like mesocrystals were synthesized by a microemulsion-mediated route. The synthesis of spherical CaMoO₄ nanocrystals was reported by pulsed laser ablation in deionized water and the crystalline phase, particle morphology, particle size distribution, and photoluminescence (PL) properties were investigated. The nanosized CaMoO₄ powders were prepared by the polymeric precursor method and the photoluminescence emission was studied at room temperature.

We report here a new synthesis method, namely a surfactant-free hydrothermal route, for controllable synthesis of CaMoO₄ hierarchical nanostructures and their self-assembly into interesting erythrocyte-like nanostructures. The effects of the fundamental experimental parameters including reaction time, temperature and DMAc to H₂O ratio are investigated in detail on the formation of the calcium molybdate products. The as-synthesized products are characterized using X-ray powder diffraction, scanning electron microscopy, Brunauer–Emmett–Teller and transmission electron microscopy. Finally, photoluminescent properties are studied for the erythrocyte-like CaMoO₄ nanostructures.

Experimental

All the chemicals were of analytical grade and utilized without further purification. In a typical synthesis route, 1 mmol anhydrous CaCl₂ was dissolved in 35 mL of N,N-dimethylacetamide (DMAc)-H₂O solution at a volume ratio of DMAc:H₂O = 14.3:85.7 and the obtained solution was sonicated in an ultrasonic bath to form a clear solution. The solution was then transferred to a Teflon-lined stainless steel autoclave and heat-treated at 180 °C for 72 h under an autogenous pressure. After cooling to room temperature, the obtained products were collected by filtration and washed with deionized water and ethanol. The obtained powder was finally dried at 80 °C in a vacuum oven.

†Electronic supplementary information (ESI) available: Fig. S1: comparison of human erythrocytes and erythrocyte-like CaMoO₄; Fig. S2: time-dependent morphological evolution of CaMoO₄; powder XRD of CaMoO₄; Fig. S4 and S5: SEM images of CaMoO₄. See DOI: 10.1039/b915099d
water bath for 30 min. Then, 1 mmol (NH₄)₆MoO₂₄·4H₂O was added to the above solution. The mixture was placed in a 40 mL Teflon-sealed autoclave and maintained at 180 °C for 30 min. After cooling to room temperature, the product was separated from the solution by centrifugation, washed several times with alcohol, and then dried in air at 70 °C. To investigate the intermediates, CaMoO₄ products were also obtained at different reactive stages during the synthesis process. In addition, CaMoO₄ products were also synthesized for different lengths of time in order to study the effect of reaction time on the morphological evolution of the CaMoO₄ products.

The phase purity of the products was characterized by X-ray powder diffraction (XRD) using an X-ray diffractometer with Cu Kα radiation (λ = 1.5418 Å). Scanning electron microscopy (SEM) images and X-ray energy dispersive spectroscopy (EDS) analyses were obtained using a HITACHI S-4300 microscope (Japan). Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM) observations were carried out on a JEOL JEM-2010 instrument in bright field and on a HRTEM JEM-20010F instrument (operated at 200 kV), respectively. The surface area was measured using a Micromeritics (NOVA 4200e) analyzer. The nitrogen adsorption and desorption isotherms were obtained at 77 K using the Brunauer–Emmett–Teller (BET) method. The BET surface area was calculated from the linear part of the BET plot. Room temperature photoluminescence (PL) spectra were recorded on an F-4600 (Hitachi) spectrophotometer.

**Results and discussion**

Erythrocyte-like CaMoO₄ hierarchical nanostructures were synthesized by the reaction between Ca²⁺ and MoO₄²⁻ ions in a DMAc–H₂O system at a ratio of 14.3 : 85.7 (namely about 1/6) at a temperature of 180 °C for 30 min. The XRD pattern of the erythrocyte-like CaMoO₄ products is displayed in Fig. 1(a). All of the diffraction peaks can be indexed to the tetragonal scheelite structure with cell parameters of a = 5.19 Å and c = 11.25 Å, which is consistent with the values in the standard card (JCPDS card No. 29-0351). No impurity peaks were detected in the experimental range, thus indicating the formation of pure CaMoO₄ products. The as-prepared products were also determined by EDS analysis under N₂ atmosphere. The EDS result shown in Fig. 1(b) demonstrates that the as-prepared CaMoO₄ products contain C, Ca, Mo, Au and O. The Au-element is induced by the spattering of Au nanoparticles used for the SEM samples and the C-element is also discovered probably due to the insulating tape for adhesive samples. In addition, the atomic ratio of Ca, Mo and O is nearly 1 : 1 : 4, which agrees with the standard stoichiometric composition.

Fig. 2(a)-(c) shows the SEM images of the as-synthesized CaMoO₄ products at low, medium and high magnifications, respectively. Fig. 2(a)-(c) clearly demonstrates the formation of erythrocyte-like CaMoO₄ crystals with a high yield. Single CaMoO₄ erythrocytes have a diameter ranging from 4 to 5 μm and a thickness of about 1.5 μm. Moreover, almost all of them possess the same morphology with uniform sizes (Fig. 2(a) and (b)). In addition, the surface of the CaMoO₄ products is quite rough. Further observation (Fig. 2(c)) depicts that each erythrocyte is made up of many nanoplatelets. Careful examination reveals that the CaMoO₄ nanoplatelets are about 15 nm in thickness.

To get further information about the microstructure of these erythrocyte-like CaMoO₄ hierarchical nanostructures, the products were further investigated by HRTEM. In Fig. 2(d), the edge and center of the erythrocyte show strong brightness contrast, further confirming their erythrocyte nature. To observe the inner structures of erythrocyte-like CaMoO₄ nanostructures, the samples were sonicated vigorously for 30 min and a few broken samples were obtained, which verifies that the CaMoO₄ hierarchical erythrocytes are self-organized from small nanoplatelets as shown in Fig. 2(e). Fig. 2(f) is a lattice-resolved HRTEM image taken from a nanoplatelet. The clearly resolved lattice fringes are 0.28 nm, corresponding to the (200) plane of tetragonal CaMoO₄, which is in accordance with the SAED result (Fig. 2(g)). The selected area electron diffraction (SAED) can be indexed to a pure tetragonal phase (scheelite). The appearance of periodic diffraction spots indicates that these nanostructures are self-assembled into highly...
oriented aggregates and diffract as a single crystal (Fig. 2(g)). It is worth mentioning that the high density defects were also observed for the nanoplatelets as revealed in the image. Since the building unit nanoplatelets come from a lot of 0D subunit nanoparticles, the slight mismatching cannot be entirely avoided.

On the other hand, SEM images of the CaMoO₄ erythrocytelike nanostructures were also provided at various angles (Fig. 3), showing all sides of the as-prepared erythrocyte-like CaMoO₄ hierarchical nanostructures. The as-prepared erythrocyte-like CaMoO₄ products have exactly the same biconcave shape as human erythrocytes (see ESI, Fig. S1†).

![Fig. 3 SEM images of the erythrocyte-like CaMoO₄ hierarchical nanostructures at various angles: (a) declivitous, (b) aequilivous, (c) vertical, (d) level, (e) left-oblique and (f) right-oblique.](image)

To understand the formation process of the erythrocyte-like CaMoO₄ hierarchical nanostructures, we carried out time-dependent experiments and samples were collected at different time intervals. When the solution containing Ca²⁺ and MoO₄²⁻ ions were mixed for 5 min at 180 °C, the equiaxial CaMoO₄ nanoparticles with diameters ranging from 30 to 200 nm (the inset of Fig. 4(a)) were formed as shown in Fig. 4(a). Fig. 4(b) shows the morphology of the products synthesized under the reaction time of 15 min, the platelet-like CaMoO₄ nanostructures were obtained. When the reaction was prolonged to 30 min, well-defined erythrocyte-like CaMoO₄ nanoarchitectures were produced (Fig. 4(c)). As the reaction proceeded to 1 h, the CaMoO₄ products grew in size and part of the nanoplatelets started to dissolve into the solution and generated a lot of fragments in the solution with ill-defined erythrocyte-like CaMoO₄ architectures (Fig. 4(d)). After a reaction time of 6 h, the size of the platelet structures gradually grew, and the morphology of the nanoerythrocytes became loose with fine hierarchical nanoarchitectures (Fig. 4(e)). After a reaction time of 12 h, a large amount of porous nanoerythrocytes developed (Fig. 4(f)). When the reaction time was up to 24 h or 48 h, upon comparison of ESI Fig. S2† with Fig. 4(f), the size and morphology of the products undergo no obvious change on prolonging the reaction time. The corresponding XRD patterns of the erythrocyte-like CaMoO₄ products at different time intervals are also displayed in the ESI Fig. S3.† All of the diffraction peaks can be indexed to the tetragonal scheelite structure with cell parameters of $a = 5.19$ Å and $c = 11.25$ Å, which is also consistent with the values in the standard card (JCPDS card No.29-0351). Moreover, Fig. S3 (ESI†) shows that the crystalline degree becomes higher as the reaction time is increased.

![Fig. 4 Time-dependent morphological evolution of the CaMoO₄ products at different growth stages: (a) 5 min, (b) 15 min, (c) 30 min, (d) 1 h, (e) 6 h, (f) 12 h.](image)

In the formation process, time was the most important controlling factor. By quenching at different stages, we could easily obtain four kinds of samples: (1) nanoparticles, (2) nanoplatelets, (3) well-defined erythrocyte-like nanoarchitectures and (4) porous erythrocyte-like nanoarchitectures. The crystal growth mechanisms in solution are so complicated that the actual growth process is still largely unclear. Among the crystal growth mechanisms in solution, the Ostwald ripening, selective polymer adsorption, nucleation–dissolution–recrystallization and oriented attachment etc. were usually adopted to account for the process of crystal growth. From our experimental results, it is reasonable to presume that the formation of erythrocyte-like CaMoO₄ hierarchical nanostructures is based on the oriented aggregation mechanism. In the first stage, when the reaction was carried out in the hydrothermal system at 180 °C for a short time (5 min), it directly yielded CaMoO₄ nanoparticles, which were formed in solution through a homogeneous nucleation process. In the following secondary growth stage, the primary particles are aggregated into nanoplatelets via a process known as oriented growth. As the reaction process continues, the erythrocyte-like nanostructures of CaMoO₄ were formed via a self-assembly process between the building blocks of nanoplatelets. In the last stage, the architectures have no obvious change in size and morphology on prolonging the reaction time. We presume that the self-assembly through oriented aggregation is the non-equilibrium kinetic growth process, and that appropriate reaction conditions are necessary for the formation of erythrocyte-like architectures. Thus, the perceivable reason for the morphological transition of CaMoO₄ is that, with an increase in the size of nanoplatelets, the layers of the building blocks may decrease; parts of the nanoplatelets are destroyed and start to dissolve into the solution, which provided growth units for further growth of CaMoO₄ nanoplatelets. On the basis of the above discussion, it is suggested that the formation of erythrocyte-like CaMoO₄ hierarchical nanostructures may result from the crystal growth mechanism “oriented attachment” in terms of Ostwald
ripening. In particular, the oriented attachment mechanisms have recently been reviewed. The driving force for the so-called Ostwald ripening process is the surface energy reduction. In this process, the formation of tiny crystalline nuclei occurs first in a supersaturated medium and then is followed by crystal growth. The larger particles will then grow at the cost of the small ones due to the energy difference between the large particles and the smaller particles based on the Gibbs–Thompson law. For example, three-dimensional nanoarchitectures are formed by the oriented aggregation of CuO nanoparticles and one-dimensional orientation in the early stages of aggregation in the [001] plane of CuO nanoparticles which is followed by the formation of single-crystalline nanostructures consisting of hundreds of oriented nanoparticles. The whole evolution process for the as-prepared erythrocyte-like CaMoO₄ hierarchical nanoarchitectures is thereby illustrated in Fig. 5 in terms of the above analysis.

A control experiment study was also conducted as the value of \( \omega \) (volume ratio of DMAc to H₂O) changed. The results show that the final morphology of the CaMoO₄ products is strongly affected by the value of \( \omega \) as shown in the ESI, Fig. S4.† The DMAc–water mixture can be considered to act as a sort of template for the growth of CaMoO₄ products. Herein, we must emphasize that the low molecular liquid amide, for example, N,N-dimethylacetamide (DMAc) or N,N-Dimethylformamide (DMF), is well-known for its high synthetic value, to a large extent due to its wide liquid temperature range, good chemical and thermal stability, high polarity and wide solubility range for both organic and inorganic compounds. This uniquely versatile and powerful chemical has been used as a solvent in a wide variety of synthetic procedures, including: preparation of colloids, synthesis of block-copolymers, and many types of organic chemistry reactions. In our system, the DMAc is used as a solvent and reaction medium. We speculate that upon adding an amount of DMAc to the reaction solution, the polarity of solution will be changed under the hydrothermal conditions. Fig. S4 (ESI†) shows the SEM images of the as-synthesized products obtained at the different values of \( \omega \), respectively. It is clear that the morphology of the products critically depends on this volume ratio. The SEM images reveal that the morphology of the as-synthesized products changed gradually with a decreasing \( \omega \) value. For \( \omega = 6 \), some amorphous nanostructures are observed in the products (ESI, Fig. S4(a)†). When the \( \omega \) value is decreased to 4/3 (ESI, Fig. S4(b)†) we find that various different morphologies and structures were obtained, including platelets, spheres, and polyhedron etc. When the \( \omega \) value is decreased to 3/4, the product was mainly composed of ill-defined erythrocyte-like nanostructures (ESI, Fig. S4(c)†). Moreover, a small number of partially dissolved nanoparticles were also found. When the \( \omega \) value is decreased to 1/6, the nanoerythrocytes with a diameter of about 4–5 μm are the exclusive products as shown in Fig. 2(a)–(c). However, when the value of \( \omega \) is decreased to 0, namely the synthesis of CaMoO₄ crystals in the absence of DMAc, the experimental results indicate that microspheres with a diameter of ~3 μm were obtained (ESI, Fig. S4(d)†). Therefore, it is clear that the molar ratio of DMAc to H₂O is another important factor for the formation of CaMoO₄ products with different morphologies. Moreover, dimethylformamide (DMF) has also been used as a reducing agent in many synthetic procedures. For example, DMF has been used as a reducing agent to fabricate metal nanoparticles, e.g. Au and Ag. Nonetheless, the reducing role of DMF is larger than DMAc. Therefore, it could be speculated that the mixture of metal Mo nanoparticles and CaMoO₄ nanoarchitectures may be discovered if DMF instead of DMAc was used in the present work.

In addition to the reaction time and the volume ratio of DMAc to H₂O mentioned above, the formation of the hierarchical nanoarchitectures has also been found to be strongly dependent on the temperature. In the present work, if the reactions were performed at a lower temperature (160 °C), the images reveal that just large numbers of nanoyarns formed (ESI, Fig. S5(a)†); when the experiment was conducted at a high temperature (200 °C), the ill-defined fragment-like CaMoO₄ architectures were obtained (ESI, Fig. S5(b)†). These results confirm that the hierarchical nanoarchitectures can only be formed and stabilized under certain circumstances.

Nitrogen adsorption–desorption measurements were conducted to characterize the BET surface area and internal pore size distribution. The recorded adsorption and desorption isotherms for the erythrocyte-like CaMoO₄ nanostructures show a significant hysteresis (Fig. 6(a)). The BET surface area for the as-obtained samples calculated from the linear part of the BET plot is about 5.8 m² g⁻¹, which is lower than that for other CaMoO₄ products at a reaction time 6 h (6.0 m² g⁻¹) and 12 h (6.4 m² g⁻¹), respectively (Fig. 6(b) and (c)). This confirms that the former product has comparatively compact structure with fine pores as shown in Fig. 3 while the latter two products have a loose structure with large pores as shown in Fig. 4(e)–(f).

As we know, metal molybdate belongs to the scheelite family and is isostructural with the well-known phosphor metal tungstate. In this study, the photoluminescence emissions of the erythrocyte-like CaMoO₄ hierarchical architectures synthesized under the hydrothermal conditions at 180 °C were evaluated using 325 nm UV excitation at room temperature. The spectra are shown in Fig. 7. For the purpose of comparison, the photoluminescent (PL) properties of the CaMoO₄ products synthesized for different reaction times were also studied. The spectra show that the emission peaks centered around 469 nm and 494 nm of all the samples are observed, respectively. This is mainly attributed to the charge-transfer transitions within the MoO₄²⁻ complex. Generally, for the similar morphological samples, the better crystallized products must be more favorable to luminescent characteristics. It is thus naturally observed that the emission intensities after aging for a longer time are higher than after aging for a shorter time as depicted in Fig. 7 since the products after aging for a longer time show the better crystallization than for a shorter time as depicted in Fig. 3.

Fig. 5  Schematic illustration of the formation and shape evolution of CaMoO₄ nanoerythrocytes in the whole synthetic process.

Fig. 2(a)–(c)
concluding that the morphology, crystallization degree and configuration of the CaMoO₄ products all have effects on their luminescence properties.

Conclusions

In summary, novel erythrocyte-like CaMoO₄ hierarchical nanostructures have been successfully synthesized via a simple surfactant-free hydrothermal route by controlling the fundamental experimental parameters including reaction time, temperature and DMAc to H₂O volume ratio. Well-defined erythrocyte-like CaMoO₄ hierarchical nanostructures with a compact structure have been obtained under a reaction temperature of 180 °C for 30 min at a proper volume ratio of DMAc : H₂O = 14.3 : 85.7 while similar products with loose structures could be synthesized under similar conditions at a longer reaction time. From the experimental results, the oriented aggregation mechanism is proposed for the organization of the erythrocyte-like CaMoO₄ hierarchical nanostructures. Luminescent properties of the CaMoO₄ nanoerythrocytes have been studied and the erythrocyte-like CaMoO₄ nanostructures showed a strong blue emission. The present study could provide an easy surfactant-free synthetic route for the controllable construction of inorganic materials with high hierarchy in the absence of any surfactants.

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