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Biomolecule-assisted route for shape-controlled synthesis of 3D flower-like $CdWO_4$ microstructures

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Uniform 3D hierarchical flower-like $CdWO_4$ microstructures have been conveniently synthesized by using sodium cholate as a self-assembly facilitating agent at low temperature (35 ^{o}C). The flower-like $CdWO_4$ microspheres are composed of radiatively assembled monoclinic-crystalline $CdWO_4$ nanoplates with lengths of several hundred nanometers. It is noted that the introduction of sodium cholate can make the preparation of 3D $CdWO_4$ microspheres at much lower temperature than that of hydrothermal treatment method. The morphological modulation of the products could be easily realized by controlling the reaction temperature, reaction time, dosage of sodium cholate, and concentration of cadmium-cholate precursors. Based on the characteristic results, a possible formation mechanism of 3D flower-like $CdWO_4$ microspheres was proposed.

Introduction

Over the past decade, morphology-controlled synthesis of inorganic nano/micromaterials has attracted considerable attentions due to their excellent properties and fundamental significance in a wide variety of application fields,[1-9] including catalysis, optics, electronics, magnetism, sensors, biology and drug delivery et al.[10-12] Extensive work has been devoted to the development of effective methods to synthesize functional materials with complex three-dimensional (3D) hierarchical architectures, such as Fe_2O_3 flower-like microspheres,[13] urchin-like WO_3 and $MnWO_4$ microstructures,[14-15] cactus-like β-Ga_2O_3 microarchitectures,[16] dandelion-like ZnO and CuO architectures,[17-18] 3D hierarchical MWO_4 (M=Mn, Bi, Ba, Pb) and $MMoO_4$ (M=Fe, Pb, Ba) superstructures,[19-27] hyperbranched $BiVO_4$ hollow cages,[28] have been fabricated from low dimensional nanobuilding units by bottom-up approaches. Nevertheless, most of the synthetic procedures always need high temperature treatment.

Cadmium tungstate ($CdWO_4$) with the monoclinic wolframite structure is one of the most promising multicomponent metal oxide nanomaterials, which exhibits remarkable potential as X-ray scintillators[29-30] and advanced medical X-ray detectors in computerized tomography.[31] Specifically, the well-ordered 1D, 2D, and 3D hierarchical $CdWO_4$ structures with improved physical/chemical properties may found wide range of applications in photoluminescence, scitillators and photocatalysis.[32-34] It has been well demonstrated that $CdWO_4$ 1D nanorods,[35] nanobelts,[36] nanobundles[37] and 2D nanofilms[38] can be synthesized conveniently by chemical reaction in a molten salt solution and high-temperature thermal treatment processes. However, the synthesis of 3D hierachical $CdWO_4$ structures is rarely reported,[39] not to mention the development of facile and effective low temperature synthetic strategies for the fabrication of well-ordered 3D $CdWO_4$. It is demonstrated that the low-temperature synthesis of 3D hierarchical nano/microstructures is significant to their large-scale applications.[40-41] In this respect, amiphiphilic molecular-assisted assembly may provide a powerful low temperature tool for the synthesis of hierarchical nano/micrometer structures.

In this paper, we provide a facile and effective route for shape-controlled synthesis of 3D flower-like $CdWO_4$ microstructures with the help of sodium cholate (SC), which is a naturally occurring biodegradable amiphiphilic molecule and has been widely exploited in the fabrication of morphology-controlled synthesis of nanomaterials.[42-43] Unlike the previous reports on the preparation of $CdWO_4$ nano-/micromaterials by high temperature (>100^{o}C) hydrothermal treatment method, the well-organized flower-like architectures can be fabricated conveniently in very low temperature (35^{o}C). Through the delicate tuning of the preparation conditions such as the synthesis temperature, synthesis time, the dosage of SC, the morphology of the 3D architectures can be finely adjusted. The assembly mechanism of 3D hierarchical microstructures have also been investigated.

Experimental

Synthesis

All chemicals and solvents used were of analytic grade without further purification unless specially stated. In a typical synthesis, 10 mM of cadmium nitrate tetrahydrate ($CdN_2O_6{\cdot}4H_2O$) and 10 mM of SC were mixed in aqueous

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solution to obtain the cholate and cadmium nitrate mixtures. The resulting mixture was kept under static condition for 48 h in a thermostatic water bath, the reaction temperature varied from 25 to 65 °C. Then, $Na_2WO_4 \cdot 2H_2O$ aqueous solution was added into the above mixture in a 1:1 molar ratio (Cd:W). White precipitates were gradually formed. After the reaction was completed, the white precipitates were collected by centrifugation and washed with distilled water and ethanol for three times. Finally, the products were dried at 60 °C. The yield of the 3D flower-like $CdWO_4$ microstructures was calculated to be 87%.

Characterization

The synthesized samples were characterized on a German Bruker D8 X-ray powder diffractometer Cu Kα radiation. The morphology of $CdWO_4$ microstructures were examined with a Hitachi S-4800 field emission scanning electron microscope (FE-SEM). The transmission electron microscopy (TEM) image was measured by a Tecnai F20 S-TWIN. Energy-dispersive X-ray spectroscopy (EDS) analysis was performed on the same FE-SEM microscope. Nitrogen adsorption-desorption isotherms were measured on a Quantachrome instrument (NOVA 2200e). The surface areas and the pore size distributions were calculated using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods, respectively. The X-ray photoelectron spectra (XPS) were taken on a 400KCPS XPS spectrometer equipped with an Al Ka X-ray source. The photoluminescence (PL) measurements were performed on a fluorescence spectrophotometer (Hitachi F-4600) equipped with a continuous 150W Xe-arc lamp.

Results and discussion

Characterization of flower-like $CdWO_4$ microstructures

The $CdWO_4$ microstructures were prepared by a facile and efficient low temperature process by using $Na_2WO_4 \cdot 2H_2O$ as the tungsten source, $Cd(NO_3)_2 \cdot 4H_2O$ as the cadmium source and biosurfactant SC as the assistant of the formation of supramolecular microstructures. The XRD pattern of a typical sample prepared at 35 °C for 24 h with cadmium/tungsten in a molar ratio of 1:1 is shown in Fig. 1a. All the diffraction peaks can be indexed to the high purity, well crystalline, monoclinic structure of $CdWO_4$ with lattice parameters of *a*= 5.029Å, *b*= 5.859Å, *c*= 5.074 Å and a space group of *P2*/c (Joint Committee on Powder Diffraction Standards JCPDS No. 14-0676).

The morphology of $CdWO_4$ products prepared under the above mentioned conditions were studied by SEM. Fig. 1b shows that the sample composed of abundant uniform 3D flower-like microspheres with diameters of about 2~3 μm. The as-obtained flower-like microstructures could not be destroyed and broken into discrete nanoplates even by subjecting their aqueous suspensions to ultrasonication, indicating that the microstructures were not a random aggregate of nanoplates but the well-organized assemblies. An SEM image at higher magnification shows that these $CdWO_4$ microstructures were assembled from 2D willow leaves-shaped nanoplates (about 10-20 nm in thickness) in a radiative way (Fig. 1c). To further investigate the characteristics of the flower-like $CdWO_4$ microarchitectures, TEM technique was employed. As shown in Fig. 2a-c, the diameter of the $CdWO_4$ microarchitecture is c.a. 2~3 μm. $CdWO_4$ nanoplates with lengths of several hundred nanometers and widths of c.a. 100 nm densely assembled in a radiative way from the center to the surface of the microarchitecture (Fig. 2a). Several $CdWO_4$ nanoplates broken from the microarchitectures are shown in Fig. 2c. The high-resolution TEM (HRTEM) image (Fig. 2d) recorded from the terminal part of an individual nanoplate marked by a yellow rectangle shows two sets of crystal lattice fringes. And the spacing between two adjacent crystal lattice fringes is 5.0 Å and 2.5 Å, corresponding to that of the (100) and (002) planes of the monoclinic $CdWO_4$ phase respectively. The selected area electron diffraction (SAED) pattern (Fig. 2e) clearly displays a set of diffraction spots, further indicating the single crystalline nature of the $CdWO_4$ nanoplates. By comparing the HRTEM image and its corresponding SAED pattern, it is confirmed that the growth direction of $CdWO_4$ nanoplates is the [001] direction.

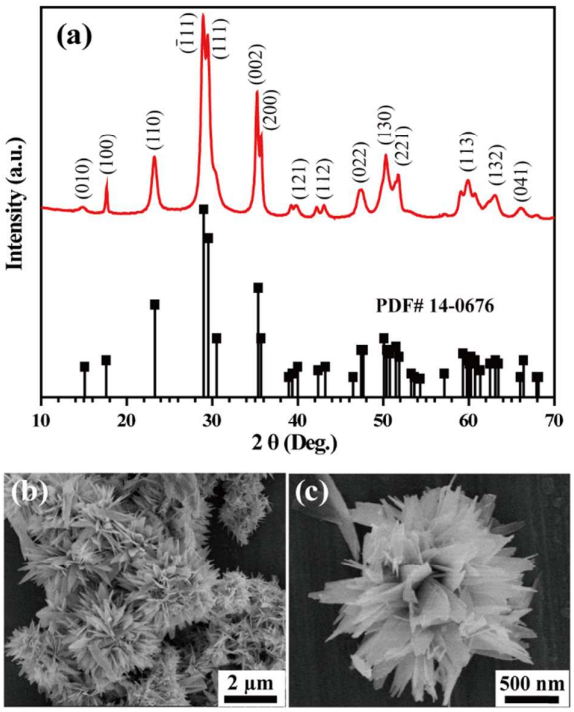

Fig. 1 XRD pattern (a) and SEM images (b-c) of the sample prepared at 35 °C for 24 h with cadmium/tungsten in a molar ratio of 1:1.

Effects of synthesis temperature

The preparation conditions, such as the preparation temperature, the dosage of SC, and the reaction time, all play crucial roles in the fabrication of tungstates structures with controlled morphologies. In our study, the synthesis temperature is varied from 25 °C to 65 °C to investigate its effects on the structure and morphology of $CdWO_4$ products, while the SC/cadmium concentration is fixed at 10

mM/10 mM and the reaction time is kept at 24 h in the synthesis procedure. As revealed by the XRD patterns (Fig. S1), monoclinic $CdWO_4$ phase (JCPDS card no. 14-0676) can be obtained under the whole series of synthesis temperature (25~65 °C) with the assistance of SC. And no impurities can be found in the XRD patterns. Under careful observation, it is found that the XRD pattern exhibits a slightly broad diffraction peak when the reaction temperature is 25 °C, indicating the poor crystallinity of sample. When the reaction temperature ranges from 35 °C to 65 °C (slightly higher than room tempreature), the width of diffraction peaks gets narrowed and the peak position and intensities did not changed distinctively, suggesting that the high quality monoclinic $CdWO_4$ phase can be obtained conveniently in our experiment. Compared to the traditional hydrothermal method,[44-47] this biosurfactant assisted synthetsis of monoclinic $CdWO_4$ can be carried out at very low temperature.

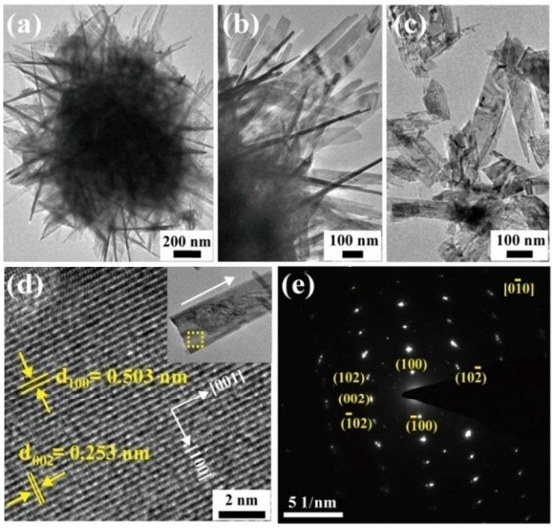

Fig. 2 (a, b, c) TEM images, (d) HRTEM image, and (e) SAED pattern of the sample prepared at 35 °C for 24 h with cadmium/tungsten in a molar ratio of 1:1.

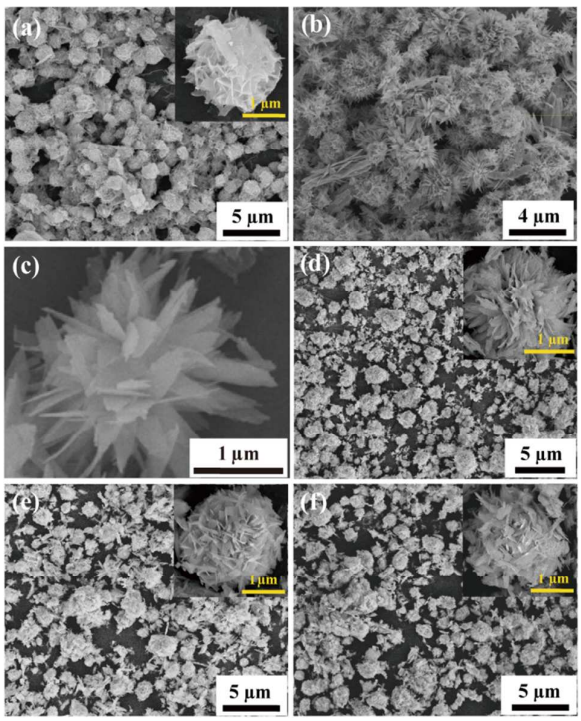

Fig. 3 SEM images of the samples prepared at different reaction temperature for 24 h in the assistance of SC, (a) 25 °C, (b-c) 35 °C, (d) 45 °C, (e) 55 °C, and (f) 65 °C.

Fig. 3a-f display the SEM images of $CdWO_4$ products obtained at the temperature of 25~65 °C. At 25 °C, the hierarchical microspheres with a narrow size distribution (2-3 μm) are obtained. Most of the microspheres are sticking together and composed of irregular nanosheets, which assembled into a closed flower-like hierarchical microstructures (Fig. 3a). As the synthesis temperature increased to 35 °C, well-defined flower-like $CdWO_4$ microstructures with uniform diameters (c.a. 3 μm) were formed. The 3D hierarchical open flower-like structures are composed of willow leaves-shaped nanoplates, which is found similar to the small fraction of dispersed nanoplates under higher magnifications (Fig. 3b-c). It is verified that the flower-like $CdWO_4$ microstructures were assembled by the willow leaves-shaped nanoplates in a radiative way. At the synthesis temperature of 45 °C, the "leaves" of the flower-like microstructures becomes smaller, the compaction of the "leaves" in the radiative way becomes much condensely, the sizes distribution of these microspheres becomes broader (sizes in the range of 1-5 μm) (Fig. 3d). When the synthesis temperature is further raised to 55 °C and 65 °C, the uniform radiative flower-like microstructures transformed into 3D microspheres with building blocks randomly organized and a wide size distribution (several hundred nanometers to 6 μm, Fig 3e-f). When the temperature was promoted, the reaction rate and the growth of 3D structures were accelerated, which was disadvantageous for the well-ordered growing of the building blocks and thus might lead to the irregularity of assembly morphology and the wide size distribution of the 3D microspheres.[48-49] From the SEM images of the products, it can be seen that the most appropriate synthesis temperature to obtain the uniform 3D hierarchical flower-like microstructures is at 35 °C.

Effects of synthesis time

In order to further investigate the formation mechanism of the 3D flower-like $CdWO_4$ microstructures, a series of time-dependent experiments has been performed at 35 °C with fixed concentration of SC/cadmium source/tungsten source (10 mM/10 mM/10 mM). Under this condition, the solid precipitates can be obtained as soon as the addition of tungsten source to the SC-cadmium complex systems. From the SEM images as shown in Fig. 4, it can be seen that both the dispersed nanoplates and nanobundles can be obtained after treated for 1 h. When the reaction time is prolonged to 3 h, irregular microspheres with diameters of about 2 μm

composed of randomly organized nanoplates are formed. As the reaction time is prolonged to 6 h, the product evolves into 3D microspheres, which are composed of nanofibers/nanoplates aligned radially from the core to the surface of the microspheres. When the reaction time extending further to 9 h, the product appears as 3D microspheres consisted of a number of nanofibers/nanoplates in a tight, regular and radiative way. As

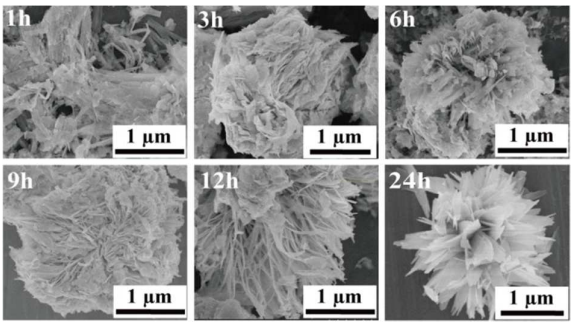

Fig. 4 SEM images of the samples collected at different reaction time in the assistance of SC.

the reaction time increases to 12 h, the morphology of the sample is similar to that of 9 h, but the space between adjacent building blocks increases. Finally, the well-defined 3D hierarchical flower-like $CdWO_4$ microspheres were formed after the reaction proceeded for 24 h. The XRD patterns of $CdWO_4$ products upon the change of reaction time were further exploited. The monoclinic $CdWO_4$ phase (JCPDS card no. 14-0676) were obtained at the initial stage and the crystal sturcture did not show obvious difference with extending the reaction time (Fig. S2). According to the above results, it can be inferred that the monoclinic $CdWO_4$ phase has been formed in the initial stage and subsequently grow anistropically to form nanofibers/nanoplates. In the assistant of amphiphilic SC, the building blocks intend to assemble to form 3D microspheres.[50] As the reaction time extended, the reaction rate slows down with the decrease concentration of the reactants. Coupled with the steric hindrance effect, the subsequent deposition of the $CdWO_4$ crystals will preferentially occur at the relatively more active sites under the kinetic control of proper conditions.[51-52] This anistropic process continues and finally leads to radiative 3D structures.

Effects of the dosage of SC

Previously, Xie and other groups have reported the hydrothermal synthesis of 3D hierarchical microstructures in the assistant of surfactants or polymers, which always need relatively high reaction temperature (over 100 °C).[53-55] In our experiment, the uniform 3D flower-like microstructures can be obtained easily at 35 °C in the assistant of biosurfactant SC. Therefore, we speculated that the existence of SC in the synthetic solution might have a crucial effect on the morphology of $CdWO_4$ samples and the effects of the dosage of SC upon the final $CdWO_4$ products have been carefully studied. The synthesis temperature is fixed at 35 °C, the reaction time is kept at 24 h and the cadmium and tungsten source concentration are both fixed at 10 mM in all the synthesis procedure, while the SC/cadmium molar ratio is varied in the range of 0-2.0.

When no SC is used, the morphology of $CdWO_4$ appeared to be irregular agglomerated nanoplate (Fig. 5a). As adding SC with different dosage, the appearance of $CdWO_4$ microstructures

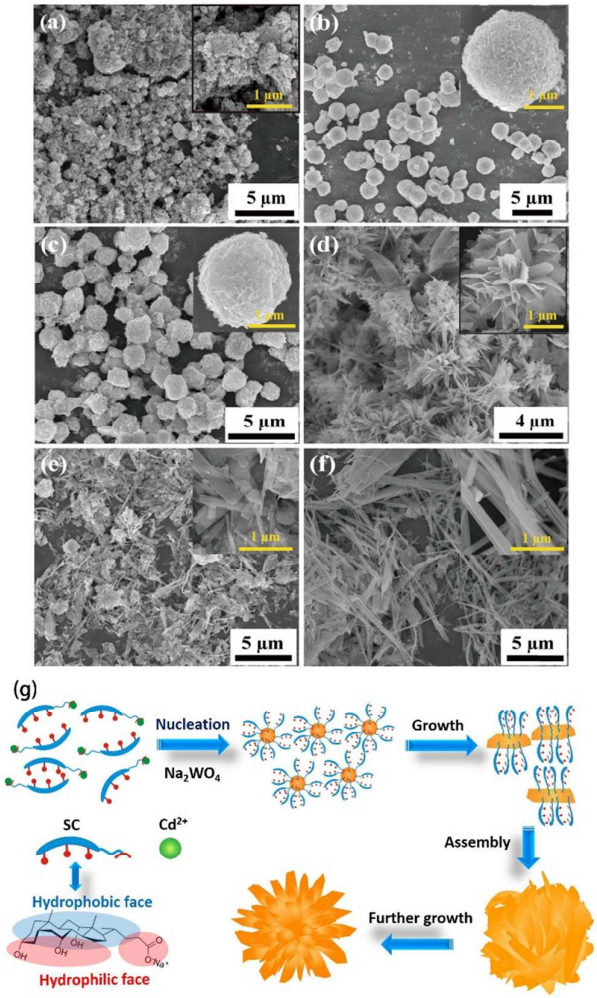

Fig. 5 SEM images of the samples prepared in different SC/cadmium molar ratio: (a) 0:1, (b) 0.1:1, (c) 0.5:1, (d) 1:1, (e) 1.5:1, and (f) 2:1; (g) plausible mechanism for the formation of 3D hierarchical flower-like structures.

changes from densely packed microspheres to radiative microflowers and finally to dispersed bundles of nanoplates (Fig.5b-f and the detailed description is displayed in supporting informatin). Particularly, when the molar ration of SC/cadmium is 1, the uniform 3D flower-like hierarchical microspheres with diameters of about 2-3 μm are obtained (Fig. 5d). An SEM image at higher magnification revealed that these $CdWO_4$ microstructures were assembled from 2D willow

leaves-shaped nanosheets (about 10-20 nm in thickness) in a radiative way.

The XPS spectrum of $CdWO_4$ products with SC/cadmium molar ratio of 1:1 (Fig. S3) demonstrated that the main peak values at 35.3 and 37.4, 404.8 and 411.5, 530.1 eV can be assigned to the binding energies of W_{4f}, Cd_{3d} and O_{1s} respectively. The two W 4f peak values were assigned to the oxidation state of W^{6+} according to the previous results.[56] For the Cd 3d XPS spectrum, the peak values at 411.5 and 404.8 were assigned to Cd $3d_{3/2}$ and Cd $3d_{5/2}$ respectively. The O 1s binding energy of 530.1 eV can be assigned to Cd-O-W bond in $CdWO_4$.[57] The quantitative analysis of this sample gave Cd, W, and O atom contents of 8.91, 6.51, and 37.29% respectively. The EDS spectrum of this sample (Fig. S5b) also revealed that most of the characterize peaks were identified as Cd, W, and O elements. The atomic percentages of Cd and W are 11.46 % and 11.68 % respectively. The Cd/W atomtic ratio is approximately 1. When no SC is used, the similar result was obtained by XPS and EDS spectrum (Fig. S4, S5a). Therefore, both the XPS and EDS results confirmed that the self-assembled flower-like microstructures and the amorphous plate-like nanostructures were composed of pure phase $CdWO_4$. The XRD patterns in Fig. S6 of the two samples further confirm the single crystalline nature of the $CdWO_4$ nano/microstructures.

From the above results, it can be seen that the dosage of SC during the synthesis procedure is critical for the morphological control of the building blocks and the overall morphology. And there exists an optimal SC/cadmium molar ratio for the preparation of the hierarchical flower-like $CdWO_4$ products.

Effects of the concentration of cadmium-cholate precursor

In our systems, the precursors of Cd^{2+} and SC complexes were obtained in the initial stage. So the concentration of cadmium-cholate precursor may also play a significant role in the formation of 3D hierarchical flower-like $CdWO_4$ microspheres. Fig. S7 shows the morphology variation of $CdWO_4$ products with the concentration of cadmium-cholate precursor adjusted in the range of 5-20 mM, while the molar ratio of Cd^{2+} to SC is fixed at 1 and reaction temperature is set at 35 ^{o}C. At the concentration of cadmium-cholate precursor is 5 mM, the product appears as microspheres, which are assembled from small irregular nanospheres/nanoplates by close packing. When the concentration of cadmium-cholate precursor is 10 mM, the well-defined 3D hierarchical micro-flowers with subunits arranged in a radiative way were formed. Further increasing the concentration of cadmium-cholate precursor to 15 mM and 20 mM, the irregular hierarchical microspheres with building blocks randomly aligned along the surface of the microspheres are formed. These results indicated that the concentration of cadmium-cholate precursor also play a role in the morphology of $CdWO_4$ 3D hierarchical microstructures.

Formation mechanism

On the basis of the above experimental results, a schematic formation mechanism of the 3D hierarchical flower-like $CdWO_4$ microspheres is proposed. As shown in Fig. 5g, SC is a facial amphiphilic biosurfactant with a hydrophilic α-face and a hydrophobic β-face. By mixing cadmium nitrate tetrahydrate with SC solution, the stable cadmium-cholate complexes were formed firstly.[42-43] Then, as adding Na_2WO_4 solution to the complexes, the facial amphiphilic cholate protected $CdWO_4$ nucleus formed presumably. In the assistance of SC, the $CdWO_4$ nucleus grow anisotropically along the <001> direction to form nanoplates, which can spontaneously assembled into 3D microstructures. The presence of cadmium-SC complexes can slow down the nucleation and subsequent anisotropic growth of $CdWO_4$, thus leads to the formation of well-ordered assembly structures.[51-52] As the reaction proceeds, the anistropic process continues and finally leads to radiative 3D flower-like microstructures.

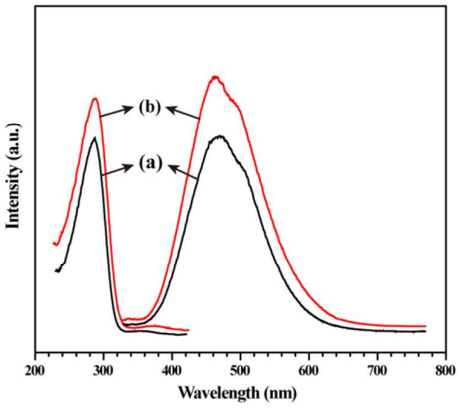

Fig. 6 Excitation spectra (left) and emission spectra (right) of $CdWO_4$ products prepared under SC/cadmium molar ratio of (a) 0:1 and (b) 1:1.

Photoluminescence study

The PL spectra of the uniform 3D hierarchical flower-like $CdWO_4$ microstructures with the assistant of SC and the irregular $CdWO_4$ nanoplates in the absence of SC are displayed in Fig. 6. When excited at 287 nm, both the samples display an emission peak centered at c.a. 460 nm, which originate from the intrinsic luminescence of tungstate group. And the emission-band shape of the $CdWO_4$ crystals is based on the $^1A_1$–$^3T_1$ transition of the $[WO_4]^{2-}$ complex anions.[39] Because both the $CdWO_4$ products composed of monoclinic crystals, so they exhibit the similar emission peaks. Differently, the 3D hierarchical flower-like $CdWO_4$ microspheres exhibited much stronger PL emission than that of bulk $CdWO_4$ materials, which can be attributed to the increased crystallinity of $CdWO_4$ crystals in the presence of SC. Our characterization studies may provide a simple new method for the synthesis of 3D ordered $CdWO_4$ materials with enhancd PL emission.

Conclusions

In summary, we developed a simple biosurfactant-assisted low-temperature assembly route to synthesize 3D flower-like hierarchical $CdWO_4$ microstructures. It is noted that the highly uniformed 3D $CdWO_4$ microstructures were assembled by highly purity of monoclinic phase $CdWO_4$ nanoplates. It is demonstrated that controlling of the experimental parameters, such as the reaction temperature, the reaction time, the dosage of SC, and the concentration of cadmium-cholate precursors all played significant roles in the morphology control of $CdWO_4$ products. Based on the characterization results, a possible mechanism was proposed to understand the formation of 3D hierarchical flower-like $CdWO_4$ microstructures. Moreover, the PL study shows that 3D hierarchical ordered microstructures exhibited great advantageous for the enhancement of PL emission. This biosurfactant assisted low temperature synthetic method may provide a useful approach for the fabrication of 3D hierarchical nano/microstructures in large-scale.

Acknowledgements

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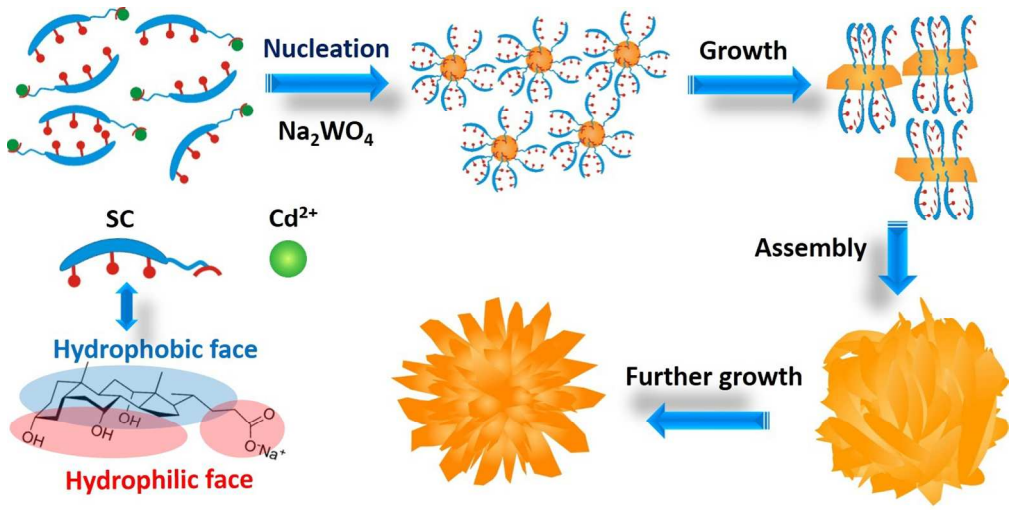

plausible mechanism for the formation of 3D hierarchical flower-like structures
250x130mm (150 x 150 DPI)