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ARTICLE

Biomolecule-assisted route for shape-controlled synthesis of 3D flower-like CdWO₄ microstructures

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Uniform 3D hierarchical flower-like CdWO₄ microstructures have been conveniently synthesized by using sodium cholate as a self-assembly facilitating agent at low temperature (35 °C). The flower-like CdWO₄ microspheres are composed of radiatively assembled monoclinic-crystalline CdWO₄ nanoplates with lengths of several hundred nanometers. It is noted that the introduction of sodium cholate can make the preparation of 3D CdWO₄ 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 CdWO₄ microspheres was proposed. High-temperature thermal treatment processes. However, the synthesis of 3D hierarchical CdWO₄ structures is rarely reported, not to mention the development of facile and effective low temperature synthetic strategies for the fabrication of well-ordered 3D CdWO₄. It is demonstrated that the low-temperature synthesis of 3D hierarchical nano/microstructures is significant to their large-scale applications.

In this paper, we provide a facile and effective route for shape-controlled synthesis of 3D flower-like CdWO₄ microstructures with the help of sodium cholate (SC), which is a naturally occurring biodegradable amphiphilic molecule and has been widely exploited in the fabrication of morphology-controlled synthesis of nanomaterials. Unlike the previous reports on the preparation of CdWO₄ nano-/micromaterials by high temperature (>100°C) hydrothermal treatment method, the well-organized flower-like architectures can be fabricated conveniently in very low temperature (35°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 anlytic grade without further purification unless specially stated. In a typical synthesis, 10 mM of cadmium nitrate tetrahydrate (Cd(NÖ₄)₂·4H₂O) and 10 mM of SC were mixed in aqueous...
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$_2$WO$_4$·2H$_2$O 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 FESEM 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 Kα 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$_2$WO$_4$·2H$_2$O as the tungsten source, Cd(NO$_3$)$_2$·4H$_2$O 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 $a = 5.029\,\text{Å}$, $b = 5.859\,\text{Å}$, $c = 5.074\,\text{Å}$ 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. 1d, 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. 1c). Several CdWO$_4$ nanoplates broken from the microarchitectures are shown in Fig. 1c. The high-resolution TEM (HRTEM) image (Fig. 1d) 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. 1e) 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.

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

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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 temperature), 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 synthesis 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.

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 nanoparticles 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

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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 extends 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 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 CdWO₄ microspheres were formed after the reaction proceeded for 24 h. The XRD patterns of CdWO₄ products upon the change of reaction time were further exploited. The monoclinic CdWO₄ phase (JCPDS card no. 14-0676) were obtained at the initial stage and the crystal structure did not show obvious difference with extending the reaction time (Fig. S2). According to the above results, it can be inferred that the monoclinic CdWO₄ phase has been formed in the initial stage and subsequently grow anisotropically to form nanofibers/nanoplates. In the assistant of amphiphilic SC, the building blocks intend to assemble to form 3D microspheres. 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 CdWO₄ crystals will preferentially occur at the relatively more active sites under the kinetic control of proper conditions. 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). 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 CdWO₄ samples and the effects of the dosage of SC upon the final CdWO₄ 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 CdWO₄ appeared to be irregular agglomerated nanoplate (Fig. 5a). As adding SC with different dosage, the appearance of CdWO₄ microstructures 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 CdWO₄ 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. For the Cd 3d XPS spectrum, the peak values at 411.5 and 404.8 were assigned to Cd 3d$_{5/2}$ and Cd 3d$_{3/2}$ respectively. The O 1s binding energy of 530.1 eV can be assigned to Cd-O-W bond in CdWO$_4$. 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 atomic 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 °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. Then, as adding Na$_2$WO$_4$ 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. As the reaction proceeds, the anisotropic process continues and finally leads to radiative 3D flower-like microstructures.

**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 $^3$A$_{2g}$$-$$^1$T$_{1g}$ transition of the [WO$_4$]$^{2-}$ complex anions. 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 enhanced PL emission.
Conclusions

In summary, we developed a simple biosurfactant-assisted low-temperature assembly route to synthesize 3D flower-like hierarchical CdWO₄ microstructures. It is noted that the highly uniformed 3D CdWO₄ microstructures were assembled by highly purity of monoclinic phase CdWO₄ nanoparticles. 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 CdWO₄ products. Based on the characterization results, a possible mechanism was proposed to understand the formation of 3D hierarchical flower-like CdWO₄ 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.

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References

plausible mechanism for the formation of 3D hierarchical flower-like structures
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