Kinetic investigation of *in situ* growth of CdMoO₄ nano-octahedra

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CdMoO₄ nano-octahedra were grown *in situ* at room temperature by reverse-microemulsion. Energy evolution from this growth process was monitored using microcalorimetry. The microcalorimetric heat flow (MCHF) curve showed a characteristic endothermic peak for the initial reaction, and double discontinuous exothermic peaks for the subsequent crystal growth. Combined with complementary characterization techniques, the evolution of morphology and size of the CdMoO₄ nano-octahedra were correlated with the MCHF peaks. Calculations based on the microcalorimetric results at 298.15 K provided rate constants of $7.56 \times 10^{-5} \text{ s}^{-1}$ for the reaction and nucleation process and $1.59 \times 10^{-4} \text{ s}^{-1}$ for the crystallization process.

***in situ* growth, CdMoO₄ nano-octahedra, microcalorimetry, heat flow curve**

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Over the past decade, attention has focused on the preparation of nanomaterials with controlled sizes and morphologies [1–3], which are important in determining the properties of the materials. Unfortunately, real time growth mechanisms for this controlled synthesis remain unclear. Consequently, clarification of the aggregation pathways and thermodynamics of *in situ* growth of nanoparticles is critical. Several methods have been used to explore the aggregation pathways during crystal growth, such as classical crystallization kinetic theory [4], *in situ* electron microscopy [5–7], scanning tunneling microscopy [8,9], *in situ* ellipsometry [10], *in situ* synchrotron X-ray absorption [11], and quartz crystal microbalance in combination with *in situ* X-ray photoelectron spectroscopy [12]. However, these methods cannot be used to evaluate instantaneous information from the non-equilibrium growth of nanomaterials. Moreover, they are expensive, carried out under harsh conditions, lack universality, and do not provide information on energetics. Thus, alternative methods are required to determine the energy evolution during synthesis of nanomaterials. This information could be used to effectively control the

size distribution, structure and growth directions of nanoparticles.

Calorimetry is an effective method to measure the changes in heat associated with crystal growth [13,14]. The major advantage of this method is that the system will not be disturbed during measurements. Additionally, continuous and accurate recordings can be provided on energy evolution in the system. *In situ* microcalorimetry has been used to systematically study the thermochemical and thermokinetic properties of the synthesis process and crystal growth of rare-earth complexes [15–17]. This method has also been applied to the zeolite and silica system, and used to delineate the relationship between thermodynamic factors and changes in the solution chemistry and interface properties [18–24]. The formation mechanism of MCM-41 mesoporous silica was also investigated using microcalorimetry [25]. In addition, microcalorimetry has been used to determine standard molar enthalpies [26] and the surface and interface enthalpies [27]. It is therefore reasonable to apply calorimetry to explore the energy evolution of other inorganic or organic nanostructure growth processes.

In this study, we used *in situ* microcalorimetry and transmission electron microscopy (TEM) to track the energy,

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morphology and size evolution of pure CdMoO_4 nanocrystallite growth from an initially clear solution. Our results can be considered in relation to a previous discussion on the growth mechanism of CdMoO_4 octahedra in terms of anisotropic growth [28]. This study aimed to investigate the energy evolution during crystal growth, and determine the interplay between thermodynamic factors. This information can provide direct experimental evidence for the fundamental forces that could be used to control crystal growth.

1 Materials and methods

1.1 Chemicals

Analytical grade $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$, $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, *n*-octanol, TritonX-100 (OP), and cyclohexane were purchased from Xilong Chemical Reagent Factory and used without further purification. Deionized water was used to prepare all the aqueous solutions.

1.2 Preparation of the initial synthesis solutions

Typically, two 13.20-mL microemulsion solutions were prepared by adding 1.20 mL 0.1 mol L^{-1} $\text{Cd}(\text{NO}_3)_2$ and 1.20 mL 0.1 mol L^{-1} Na_2MoO_4 aqueous solutions into a *n*-octanol/OP/cyclohexane system (*n*-octanol/OP/cyclohexane = 3.90:1:22.70, water contents (ω) = water/OP = 20 (molar ratio)), respectively. After 30 min of stirring, the mixture became a homogenous and completely clear solution to the naked eye, and was stored at room temperature for further use.

1.3 In situ microcalorimetric method and synthesis

The energy evolution was measured using a microcalorimeter (RD496-CK2000, MianYang CP Thermal Analysis Instrument Co., Ltd). The structure and technical parameters of this calorimeter have been detailed previously [29]. The microcalorimeter was calibrated first using the Joule effect. The sensitivities of the calorimeter were determined to be (64.54 ± 0.02) , (64.56 ± 0.03) , (64.60 ± 0.01) , (64.68 ± 0.02) , and $(64.84 \pm 0.01) \mu\text{V mW}^{-1}$ at 297.15, 298.15, 301.15, 303.15, and 308.15 K, respectively. Electric power (100 mW) was provided to the Joule cell, which had 1000 Ω electrical resistance, for 100 s at 298.15 K. The enthalpy of dissolution of KCl (spectral purity grade) in deionized water was $(17.237 \pm 0.046) \text{ kJ mol}^{-1}$, which was in agreement with an earlier measurement of $(17.241 \pm 0.018) \text{ kJ mol}^{-1}$ [30]. The calorimetric system was accurate (accuracy 0.02%) and reliable (precision 0.3%). The $\text{Cd}(\text{NO}_3)_2$ and Na_2MoO_4 microemulsions were placed in a stainless steel sample cell in separate 15-mL containers [31]. The Na_2MoO_4 microemulsion (1.0 mL) was placed in a small glass tube above the $\text{Cd}(\text{NO}_3)_2$ microemulsion (1.0 mL), which was in a larger glass tube. After establishment of equilibrium, the small

glass tube with Na_2MoO_4 microemulsion was pushed down simultaneously. This led to mixing of the two microemulsions and the thermogram was recorded.

CdMoO_4 crystals were produced as a white precipitate by reaction between the cadmium cations and molybdate anions that were solubilized in the microemulsions. Samples were removed at selected intervals and thoroughly washed with acetone, deionized water and ethanol several times to remove any impurities.

1.4 Characterization

The products were characterized by X-ray diffraction (XRD, Philips PW1710) with Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) and transmission electron microscopy (TEM, JEM-200CX, JEOL) with an accelerating voltage of 200 kV.

2 Results and discussion

2.1 In situ scanning microcalorimetry

The microcalorimetric heat flow (MCHF) curve was measured for *in situ* CdMoO_4 nanocrystallite growth at 298.15 K (Figure 1, curve Q_1). After an initial thermal disturbance caused by loading of the stainless steel sample cells, a flat segment ($t_1=0-1000 \text{ s}$) was observed, which indicates negligible thermal events occurred. The MCHF curve during this period is taken as the initial baseline for the following thermal peaks.

In curve Q_1 , one weak endothermic peak and two relatively strong and discontinuous exothermic peaks were observed simultaneously. The reaction was initiated when the two liquids mixed, and this appeared on the MCHF curve as a sharp decrease in energy with a subsequent endothermic peak. After about 30 s ($t_2=1040 \text{ s}$), the endothermic maximum was reached. Thereafter, the endothermic event rapidly changed into a more pronounced exothermic event, until at $t_3=1108 \text{ s}$ the MCHF curve crossed the baseline

Figure 1 Microcalorimetric heat flow curves of CdMoO_4 crystal growth at 298.15 K. Curves Q_1 and Q_2 were recorded in the reverse-microemulsion and aqueous solution, respectively. $Q_{0.1}$ and $Q_{0.2}$ are the base lines for curves Q_1 and Q_2 , respectively. Note that Q_2 is moved down by 0.02 mV for clarity.

from endothermic to exothermic. At $t_4=1380$ s, the exothermic peak was observed. At $t_5=4310$ s, the MCHF curve flattened and remained constant for about 5690 s. At $t_6=10000$ s, an exothermic peak began. At about 20000 s ($t_7=30000$ s), a second rough exothermic peak was observed, after which the MCHF curve flattened and remained constant for at least three more days. Therefore, formation of CdMoO_4 nanocrystals was complete at 30000 s, and the following flat curve represents the final baseline. This baseline was distinctly shifted in the exothermic direction from the initial baseline (Figure 1, curve $Q_{0,1}$). In order to understand the formation of CdMoO_4 nanocrystals, an experiment was carried out in aqueous solution. A very strong endothermic peak appeared rapidly in the MCHF curve (Figure 1, curve Q_2) as the two liquids were mixed, which was followed by a single weak exothermic peak. At $t_8=8920$ s, the MCHF curve flattened and remained flat for at least four more days. In this case, formation was complete at 8920 s, and the final baseline after this was similar to the initial baseline (Figure 1, curve $Q_{0,2}$). Thus, we can infer that the baseline shift reflects that the thermal spectra are different when the reaction takes place in different systems (aqueous vs. microemulsion). CdMoO_4 nanocrystal formation is not complete in one step when using the reverse-microemulsion synthesis and the energy of the nanocrystals is higher than that of the bulk materials.

The energy change in the reaction system depends on the reaction progress. The reaction was triggered when the reagent solutions were mixed. Based on anisotropic growth, the period from 1010–1040 s is a reaction and nucleation stage, from 1040–4310 s is the crystallization stage, and from 10000–30000 s is the crystal growth phase. For each of these processes we can determine the rate of heat production, $(dH/dt)_i$, and enthalpy, H , at time t (Table 1).

This data can be used to determine the rate constant (k) of the liquid phase reaction by the following thermodynamic equation [32].

$$\ln\left(\frac{1}{H_0} \frac{dH_i}{dt}\right) = \ln k + n \ln\left(1 - \frac{H_i}{H_0}\right), \quad (1)$$

where n is the reaction order, and H_0 is the total enthalpy of the CdMoO_4 nanocrystal growth process. At 298.15 K, the reaction and nucleation rate constant (k_1) was $7.56 \times 10^{-5} \text{ s}^{-1}$ ($R=0.997$). The crystallization rate constant (k_2) was $1.59 \times 10^{-4} \text{ s}^{-1}$ ($R=0.998$). The crystal growth stage is not a liquid phase reaction, which means eq. (1) is unsuitable, but we can investigate the enthalpy change with time (Figure 2). Linear fitting of this curve indicated that the rate of total enthalpy change (r) was $-0.1644 \text{ mJ s}^{-1}$ ($R=-0.996$) at $t=10000\text{--}30000$ s (Figure 2(a)). Obviously, the MCHF curve is not smooth in this phase, and it can be divided into three sections a, b and c with rates of enthalpy change of $r_a=-0.2415 \text{ mJ s}^{-1}$ ($R=-0.9995$) at $t=10000\text{--}14500$ s (Figure 2(b)), $r_b=-0.1890 \text{ mJ s}^{-1}$ ($R=-0.9999$) at $t=14500\text{--}15500$ s (Figure 2(c)), and $r_c=-0.1484 \text{ mJ s}^{-1}$ ($R=-0.9997$) at $t=15500\text{--}30000$ s (Figure 2(d)).

2.2 Powder XRD patterns

Figure 3 shows representative XRD patterns of the products prepared via reverse-microemulsion at room temperature. All the XRD patterns are consistent with a pure tetragonal structure for CdMoO_4 (JCPDS Card No. 07-0209). The chemical compositions of the samples were determined by energy-dispersive X-ray (EDX) spectroscopy (Figure 3 inset). The samples were found to mainly contain O, Si, Mo and Cd elements. Si signals arose from the Si substrate, and the other three element signals came from the samples.

2.3 TEM images

The formation of CdMoO_4 nano-octahedra was examined using a series of TEM images (Figure 4). These clearly revealed the crystallite structures of CdMoO_4 obtained at selected

Table 1 Thermokinetic data of the liquid-phase reaction in the reverse-microemulsion system at 298.15 K

$t(\text{s})$	Reaction and nucleation process		$t(\text{s})$	Crystallization process		$t(\text{s})$	Crystal growth process	
	$H_{1i}(\text{mJ})$	$(dH/dt)_{1i}(\text{mJ s}^{-1})$		$H_{2i}(\text{mJ})$	$(dH/dt)_{2i}(\text{mJ s}^{-1})$		$H_{3i}(\text{mJ})$	$(dH/dt)_{3i}(\text{mJ s}^{-1})$
1007	-349.9243	-0.2914	1646	-432.5462	-0.1597	14726	-3751.6672	-0.2148
1009	-352.5317	-0.3001	1666	-436.6450	-0.1637	14736	-3753.6523	-0.2143
1011	-356.0729	-0.3126	1686	-440.6772	-0.1671	14746	-3755.5354	-0.2134
1013	-359.7695	-0.3256	1706	-444.9457	-0.1712	14756	-3757.4378	-0.2127
1015	-363.2228	-0.3375	1726	-449.2196	-0.1750	14766	-3759.2844	-0.2117
1017	-366.0295	-0.3466	1746	-453.5120	-0.1785	14776	-3761.2950	-0.2115
1019	-368.4015	-0.3538	1766	-457.8453	-0.1820	14786	-3763.1096	-0.2104
1021	-370.6864	-0.3605	1786	-462.2353	-0.1854	14796	-3765.0582	-0.2100
1023	-372.6816	-0.3660	1806	-466.6684	-0.1887	14806	-3766.9161	-0.2092
1025	-374.358	-0.3701	1826	-470.9856	-0.1913	14816	-3768.8198	-0.2086
1027	-375.9267	-0.3736	1846	-475.5295	-0.1945	14826	-3770.7432	-0.2081
1029	-377.2928	-0.3763	1866	-480.0427	-0.1974	14836	-3772.464	-0.2068
1031	-378.4622	-0.3782	1886	-484.5972	-0.2003	14846	-3774.4343	-0.2066
1033	-379.4666	-0.3793	1906	-489.0816	-0.2026	14856	-3776.3870	-0.2063
1035	-380.3238	-0.3798	1926	-493.8259	-0.2058	14866	-3778.2738	-0.2058

Figure 2 Microcalorimetric heat curve of CdMoO_4 nano-octahedra at the crystal growth stage: (a) $t = 10000\text{--}30000$ s, (b) $t = 10000\text{--}14500$ s, (c) $t = 14500\text{--}15500$ s, and (d) $t = 15500\text{--}30000$ s.

Figure 3 XRD patterns of the CdMoO_4 samples obtained at reaction times of: a, 1 min; b, 30 min; c, 1 h; d, 8 h and e, 48 h.

intervals, and directly mirrored the evolution process of the morphology and size of the CdMoO_4 nanocrystals.

In combination with the MCHF curves we used the TEM results to analyze the *in situ* growth of the CdMoO_4 nanocrystals. At the end of the initial baseline (Figure 1, curve Q_1), the clear solutions were mixed together. This resulted in mixing of the Cd^{2+} and MoO_4^{2-} ions and direct precipitation of CdMoO_4 . The *in situ* MCHF curve at this point was endothermic. Near the end of the endothermic curve, the compounds started to nucleate and the MCHF curve became exothermic. Overall, the reaction and nucleation period was

Figure 4 TEM images of CdMoO_4 nanocrystals at different times during the synthesis. (a) 1 min, (b) 30 min, (c) 1 h, (d) 8 h and (e) 48 h.

characteristically endothermic. During this time, the TEM image suggests that a large number of CdMoO_4 nanoparticles form with diameters of about 15 nm (Figure 4(a)). During nucleation, the nanoparticles started to aggregate and the crystals began to grow; the curve was very exothermic at this point. This crystal growth reduced the overall interface between the solid particles and mother liquid. CdMoO_4 samples taken near the end of this phase consisted of mainly spherical and polyhedron particles with sizes of about 18 nm (Figure 4(b)). Subsequently, the *in situ* MCHF curve flattened and remained flat for about 5690 s. The heat effects during this stage were not obvious, because thermodynamic control gradually prevailed over kinetic control. This period is a homeostasis process where balance is achieved between crystal growth and dissolution. The average particle diameter in this period was 22 nm and several octahedra were observed (Figure 4(c)). The crystal growth process followed this, and anisotropic growth occurred on each plane of the crystals, which led to octahedra and similar shaped aggregates with edge lengths of about 25 nm (Figure 4(d)). Aggregation and dispersion of the crystals repelled each other strongly, slowed the reaction, which appeared on the MCHF curve as a flatter second exothermic curve compared to the first one. Finally, uniform and well-defined CdMoO_4 particles in with hemline length of 25 nm formed (Figure 4(e)). The strong brightness contrast in the image indicates that the products are nano-octahedra. The selected area electron diffraction (SAED) pattern (Figure 4(e) inset) illustrates that these nanoparticles are single crystalline CdMoO_4 structures.

3 Conclusion

In summary, microcalorimetry is a useful technique to track the *in situ* physicochemical events of nanocrystallite growth. The overall goal of our microcalorimetry study was to provide direct evidence for oscillatory thermokinetic evolution of CdMoO_4 nanocrystallite growth. On the basis of anisotropic growth, the initial process is associated with a strong energetic driving force and is controlled by chemical reactions. The remainder of the process primarily involves formation of the unique morphology, and is mainly kinetically controlled. This information aids understanding of phase transformation in inorganic composites, and could be used to control the crystal size, structures, and growth directions of nanostructure inorganic composite materials.

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