# Controlled Synthesis of Novel Flower-shaped $BaCrO_4$ Crystals

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Flower-shaped $BaCrO_4$ crystals have been synthesized via a facile polymer-mediated crystallization process at ambient temperature. A possible formation process has been proposed accounting for the formation of $BaCrO_4$ flower.

The controlled synthesis of inorganic or inorganic/organic hybrid materials with specific shape or highly ordered hierarchical architecture is a key challenge in current materials synthesis and device fabrication.[1,2] Recently, bioinspired synthesis strategies, using specific organic template or additive to regulate the nucleation, growth and alignment of inorganic materials, have been explored as a promising approach for the crystal design and morphological control of inorganic minerals.[3,4]

Currently, $BaCrO_4$ has been widely used as a model system for the study of morphological control of inorganic mineral. For example, $BaCrO_4$ nanorods and their ordered organization were obtained in AOT-based microemulsion.[5] Hierarchical tree-like superstructure of $BaCrO_4$ nanobelts were prepared in a catanionic reverse micelle.[6] Seperated $BaCrO_4$ nanofibers and hierarchical assembly of $BaCrO_4$ nanofibers[7] were synthesized in certain aqueous polymer solution. Herein, we report the controlled synthesis of $BaCrO_4$ crystals with novel flower-like morphology in the aqueous solution of poly(styrene-*alt*-maleic acid) (PSMA). To the best of our knowledge, this is the first report on the synthesis of well-defined $BaCrO_4$ flowers.

The synthesis of flower-shaped $BaCrO_4$ crystals, involving a polymer-mediated mineralization process, was performed at ambient temperature. In a typical synthesis, a solution of $Na_2CrO_4$ (0.5 M, 0.4 mL) was added into an aqueous solution of PSMA (100 mL, $1.0\,g\,L^{-1}$), and the pH of the solution was adjusted to 5–7 by using HCl or NaOH solution. Then a solution of $BaCl_2$ (0.5 M, 0.4 mL) was added quickly into the pH-adjusted solution under vigorous stirring by using a magnetic stirrer. The mixture was stirred for another 3 min, and then the solution was kept under static conditions for 24 h to ensure equilibration. In addition, the experiments were also performed to investigate the morphological change of $BaCrO_4$ products with the variation of PSMA concentration. The morphology of the resulting $BaCrO_4$ precipitates was characterized by scanning electron microscopy (SEM, JSM-5610LV), transmission electron microscopy (TEM, JOEL-2010 HT). The powder X-ray diffraction (XRD) patterns obtained on a X-ray diffractometer (HZG41B-PC) using Cu K$\alpha$ radiation at a scan rate of $0.05°\ 2\theta{\cdot}S^{-1}$ were used to examine the crystal structure.

Figure 1 shows the XRD patterns of the as-prepared samples at varying PSMA concentration, while all the other conditions, such as pH value, temperature etc, are kept the same. All the diffraction peaks can be indexed with reference to the unit cell of the hashemite structure (JCPDS No. 15-0376, $a = 9.105$, $b = 5.541$, $c = 7.343$ Å, space group: *Pnma*). However, the relative intensity of the peaks corresponding to the (111), (102), (112), (020) planes varies significantly from the literature value,[7] indicating the different tropism of the products, which may be related to the selective adsorption of PSMA on the crystal plane of $BaCrO_4$.

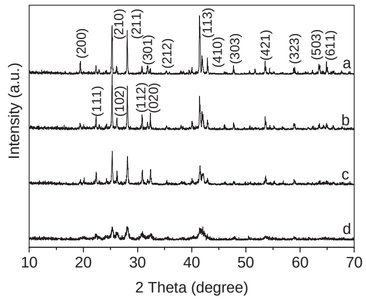

**Figure 1.** XRD patterns of the products obtained with varying PSMA concentration: (a) 0.05, (b) 0.5, (c) 1, and (d) $4\,g\,L^{-1}$.

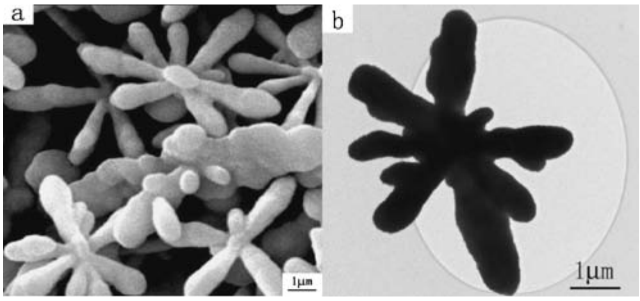

**Figure 2.** SEM images and TEM images $BaCrO_4$ flowers obtained in the presence of $1\,g\,L^{-1}$ PSMA. The related SAED patterns are shown in the supporting information.

Figure 2a is a typical SEM image of the products obtained in the presence of $1\,g\,L^{-1}$ PSMA. It shows that the products mainly consist of well-defined flower-shaped $BaCrO_4$ particles. An individual $BaCrO_4$ flower has several rod-like petals extending radically from the column-like center. Generally, those rods have increasing diameter from the center to the tip. However, the angle between two neighboring petals is discrepant with each other. The morphological feature of as-obtained $BaCrO_4$ flower is also depicted in a typical TEM image (Figure 2b). It shows that the flower seems crystallographically asymmetric, implying that the flower may be resulted from the aggregation or assembly of primary particles. The crystalline nature of the $BaCrO_4$ flower was further characterized by electron diffraction (ED). The selected areas ED (SAED) patterns[8] are recorded from different areas of a single flower. Although the SAED patterns show that every individual petal or the center is single-crystalline, they do not seem to share the same orientation, which further confirms that the as-obtained flower is an assembly of the primary crystals. In fact, an intermediate (Figure 3) for the flower has been recorded as the polymer concentration is reduced to some degree. This may give us some hints to speculate the formation process of the as-obtained $BaCrO_4$ flowers. Several leaf-like plates are self-assembled resulting in the formation of a flower-like superstructure, whose configuration is rather similar to the flower obtained under standard conditions. Therefore, a multistep formation mechanism for the $BaCrO_4$ flower has been proposed. In the first step, a primary leaf-like plate is formed. In the second step, those primary leaf-like plates assemble to form a flower-like superstructure. Finally, the petals of the flower are overgrown to form rod-like morphology, resulting in the well-defined $BaCrO_4$ flower.

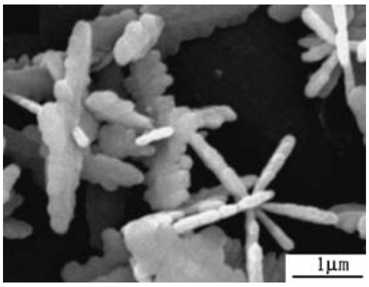

**Figure 3.** SEM image of $BaCrO_4$ flower-like superstructure consisting of leaf-like plates obtained in the presence of $0.5\,g\,L^{-1}$ PSMA.

The synthesis of the $BaCrO_4$ flower can be easily controlled, and the starting experimental conditions can be conveniently adjusted to modify the shape of the resulting products. Especially, the morphology of the $BaCrO_4$ particles is significantly changed with changing PSMA concentration.

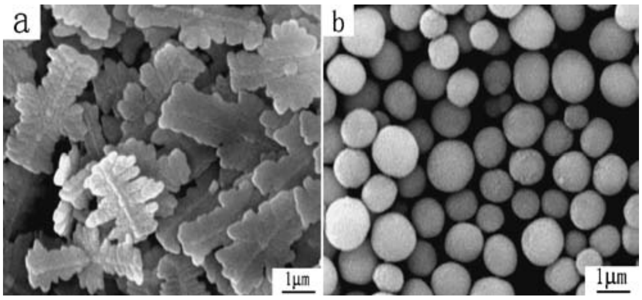

**Figure 4.** SEM images of $BaCrO_4$ leaf-like plates and spherical superstructure obtained in the presence of (a) 0.05 and (b) $4\,g\,L^{-1}$ PSMA.

The morphology of the products is transformed to homogeneous leaf-like plates (Figure 4a) when PSMA concentration is reduced to $0.05\,g\,L^{-1}$ while the other conditions are kept the same. The leaf-like plates display a special two-dimensional structure with branches growing vertically on the main truck. The branches approach each other closely in a parallel manner. Although the length of the branch at the same side is not identical, the structure on both side of the truck is greatly symmetric. On the other hand, when PSMA concentration is increased to a certain level, the products are transformed to $BaCrO_4$ spheres (Figure 4b). The rugged surface of the spheres indicates that they are composed of primary crystallites, which is further confirmed by the corresponding XRD results (Figure 1d). The mean crystallite size is estimated to be about 28.8 nm according to the Scherrer equation.

The variation of morphology with varying polymer concentration may be ascribed to the different adsorptive feature of PSMA on the crystal plane of $BaCrO_4$. It is known that the exposed faces of $BaCrO_4$ crystals show different polarity pattern and average interface energy, and thus adsorb the polymer with different efficiency.[7] At a lower concentration, the polymer just selectively adsorbs on a certain crystal face of $BaCrO_4$, leading to the anisotropic growth and directional assembly. In contrast, at a higher concentration, the polymer is enough to adsorb on almost all the crystal faces, resulting in the spherical superstructure.

In summary, $BaCrO_4$ flowers are fabricated via a facile PSMA-mediated precipitation reaction of $BaCrO_4$ from aqueous solution at ambient temperature. Furthermore, $BaCrO_4$ flowers can be transformed to $BaCrO_4$ leaflets or $BaCrO_4$ spheres by simply reducing or increasing the PSMA concentration. This facile polymer-mediated mineralization route for the formation of inorganic mineral with fascinating shape is worth being further explored for other mineral systems.

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8 See supporting information for additional details.

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