

## Morphological Control of $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$

**Andrew M. Fogg,\* Amal J. Freij, Allan Oliveira, Andrew L. Rohl, Mark I. Ogden,  
Gordon M. Parkinson,**

*A. J. Parker Cooperative Research Centre for Hydrometallurgy, School of Applied  
Chemistry, Curtin University of Technology, P.O. Box U 1987, Perth 6845, Australia.*

*E-mail: amf@power.curtin.edu.au*

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**The effect of a range of inorganic and organic crystal growth modifiers on the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  has been studied. It has been found that some additives show a strong preference for a single crystal face forming polyhedral crystals whilst others are less selective, producing crystals with a less well defined morphology. In this way sulphite and dithionite preferentially interact with the {111} face producing octahedral crystals and nitrilotriacetic acid stabilises the {110} face forming rhombic dodecahedral crystals. Phosphate, however, leads to the formation of small needle-like crystals and the organic acids,  $\text{N}(\text{CH}_2\text{CO}_2\text{H})_2(\text{CH}_2\text{PO}_3\text{H}_2)$ ,  $\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ,  $\text{HN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , and  $\text{H}_3\text{CN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , produce near spherical crystals.**

The ability to be able to control the morphology of a material is of great importance in a variety of fields. This control is brought about by varying the crystallising conditions, typically by the addition of a crystal growth modifier to the solution. For molecular crystals, morphological modification has been brought about by the use of stereospecific inhibition of the growth of particular crystal faces. [1,2]

In inorganic systems such a strategy is not generally applicable and a more empirical approach exploiting the bonding and packing in the crystal structure must be used. In this way it has proved possible to introduce crystal faces into the morphology of materials such as  $\text{CaCO}_3$ , [3]  $\text{KNO}_3$  [4] and  $\text{K}_2\text{SO}_4$  [5] that are not normally observed. In extreme cases the morphology can be so completely altered that it is comprised of a single different crystal face. For example, the growth of KCl in the presence of sodium hexametaphosphate leads to the formation of octahedral crystals ( $\{111\}$  face) rather than the usual cubic morphology ( $\{100\}$  face). [6]

In many cases the crystal growth modifier leads to the observation of more complex morphologies that do not simply consist of a combination of crystal faces. One material that has been shown to be particularly flexible in the morphologies adopted is  $\text{CaCO}_3$ . Variation of the additive used in the synthesis has led to morphologies as diverse as spheres, [7-9] helices, [10] and hollow porous shells. [11]

$\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  is the silicon free member of the garnet family of minerals, having a cubic structure in which Al is in an octahedral environment and Ca is eight co-ordinate in a square anti-prismatic arrangement. [12,13] It is an important constituent of cement [14] and a by-product of the Bayer Process. [15]

The morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  grown from basic solution is generally poorly defined though some of the smaller crystals display a 24-sided deltoidal icositetrahedral morphology. [16] In another paper we have shown the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  to be strongly dependant on the presence of crystal growth modifiers in the reaction solution. [17] It was found that in the presence of sulphate, octahedral crystals were formed by stabilisation of the  $\{111\}$  face, oxalate preferentially interacts with the  $\{110\}$  face leading

to rhombic dodecahedral crystals and EDTA with the {210} face forming crystals with a tetrakis hexahedral morphology.

### **Experimental Details**

The synthesis of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  was based on the method described previously by Whittington *et al.* [16] In a typical experiment 6.44g (0.0826mol) gibbsite was dissolved in 10mL of 13.3M NaOH solution at 95°C. 3.47g (0.0468mol)  $\text{Ca}(\text{OH})_2$ , slurried in 40mL de-ionised water, was then added to the original solution and maintained at 95°C for 24 hours. Experiments were also performed in the presence of the following crystal growth modifiers: sodium chloride, sodium sulphite ( $\text{Na}_2\text{SO}_3$ ), sodium thiosulphate ( $\text{Na}_2\text{S}_2\text{O}_3$ ), sodium dithionite ( $\text{Na}_2\text{S}_2\text{O}_4$ ), sodium phosphate ( $\text{Na}_3\text{PO}_4$ ), sodium formate ( $\text{NaCHO}_2$ ), sodium acetate ( $\text{NaCH}_3\text{CO}_2$ ), sodium succinate ( $\text{Na}_2\text{C}_4\text{H}_4\text{O}_4$ ), and the organic polyacids shown in Figure 1. In each case the additives were used as purchased except for NDMPA, NMPDA, NDP and MNDP which were synthesised according to the literature preparations. [18] In these experiments the crystal growth modifiers were added to the slurried  $\text{Ca}(\text{OH})_2$  at a concentration of 0.035 mol/L in the final solution. Powder XRD patterns of the products were recorded on a Philips PW3020 diffractometer using  $\text{Cu K}\alpha$  radiation and showed them to be  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  with a small amount of residual  $\text{Ca}(\text{OH})_2$ . No discernable changes in the diffraction patterns were observed in any of the reactions with the crystal growth modifiers. The morphology of the samples was investigated by SEM on a Philips XL30 instrument.

### **Results and Discussion**

The morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  grown in the absence of any crystal growth modifiers, shown in Figure 2, was found to be poorly defined in that no distinct crystal faces could

be identified and that the shape was not consistent throughout the sample. Our observed morphology is in agreement with that reported by Whittington *et al.* [16]. Repetition of this experiment in the presence of crystal growth modifiers such as sulphate, oxalate and EDTA showed that they have a strong influence on the experimental morphology, leading to well defined shapes comprised of a single crystal face. Full details of these experiments will be published elsewhere [17]. As an extension of this study, the effects of several other related additive anions on the morphology have been investigated in the present work, and are also found to alter the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ .

The sulphur-oxygen anions sulphite and dithionite have a similar effect to sulphate on the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  in that they lead to the formation of octahedral crystals dominated by the  $\{111\}$  face. SEM images of these crystals are shown in Figure 3(a)-(b), from which it can be seen that particularly in the case of sulphite the transformation to octahedral crystals is not uniform throughout the sample. In contrast to this, thiosulphate was not observed to have any significant effect on the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  under these conditions.

In the previous study, the carboxylate anions oxalate and EDTA were found to have significant effects on the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ . Several other carboxylate anions including formate, acetate and succinate had no observable effect on the morphology. The polycarboxylic acid, nitrilotriacetic acid ( $\text{N}(\text{CH}_2\text{CO}_2\text{H})_3$ ), did however alter the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ . In this case, the dominant crystal morphology was the rhombic dodecahedron formed by the  $\{110\}$  face and observed previously in the presence of oxalate. An SEM image of these crystals is shown in Figure 3(c). The expected

morphologies of crystals comprising the {111} or {110} faces are shown in Figure 3(d)-(e).

In all of these cases, the crystal growth modifier has targeted a single crystal face, leading to the formation of well defined polyhedral crystals. Other additive anions have, however, have led to the growth of crystals with a less well defined morphology but still significantly different to that of the  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  blank. For example, growth of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  in the presence of phosphate leads to the formation of small needle-like crystals which typically agglomerate into balls as shown in Figure 4.

The organic phosphonic acids,  $\text{HN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  and  $\text{H}_3\text{CN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , and the mixed carboxylic/phosphonic acids,  $\text{N}(\text{CH}_2\text{CO}_2\text{H})_2(\text{CH}_2\text{PO}_3\text{H}_2)$  and  $\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , each produced a near spherical morphology for  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  indicating they have a similar stabilising or inhibiting effect on each crystal face. Typical SEM images of these crystals are shown in Figure 5.

## Conclusions

We have shown that by variation of the crystal growth modifier, the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  can be carefully controlled. The experimental morphologies range from regular polyhedral crystals such as octahedra and rhombic dodecahedra grown in the presence of dithionite and nitrilotriacetic acid, respectively, to small needles when phosphate is the additive anion, and spheres with the organic acids  $\text{HN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ,  $\text{H}_3\text{CN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$ ,  $\text{N}(\text{CH}_2\text{CO}_2\text{H})_2(\text{CH}_2\text{PO}_3\text{H}_2)$  and  $\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)_2$ . The results suggest that the control of TCA6 formation and morphologies through the use of simple additives is possible.

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## References

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## Figure Captions

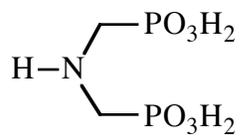
**Figure 1** Organic polyacids used as crystal growth modifiers during the preparation of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$ .

**Figure 2** SEM images of the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  grown in the absence of any crystal growth modifiers.

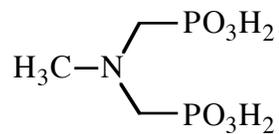
**Figure 3** SEM images of the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  grown in the presence of (a) sulphite, (b) dithionite and (c) nitrilotriacetic acid. The expected morphologies of crystals comprising (d)  $\{111\}$  and (e)  $\{110\}$  faces.

**Figure 4** SEM images of the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  grown in the presence of phosphate.

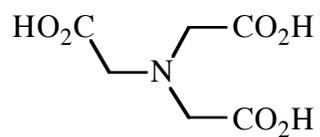
**Figure 5** SEM images of the morphology of  $\text{Ca}_3\text{Al}_2(\text{OH})_{12}$  grown in the presence of (a)  $\text{N}(\text{CH}_2\text{CO}_2\text{H})_2(\text{CH}_2\text{PO}_3\text{H}_2)$ , (b)  $\text{N}(\text{CH}_2\text{CO}_2\text{H})(\text{CH}_2\text{PO}_3\text{H}_2)_2$ , (c)  $\text{HN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$  and (d)  $\text{H}_3\text{CN}(\text{CH}_2\text{PO}_3\text{H}_2)_2$



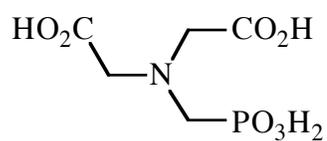
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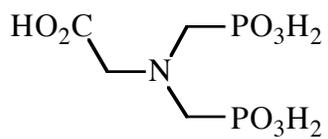
MNDP



NTA

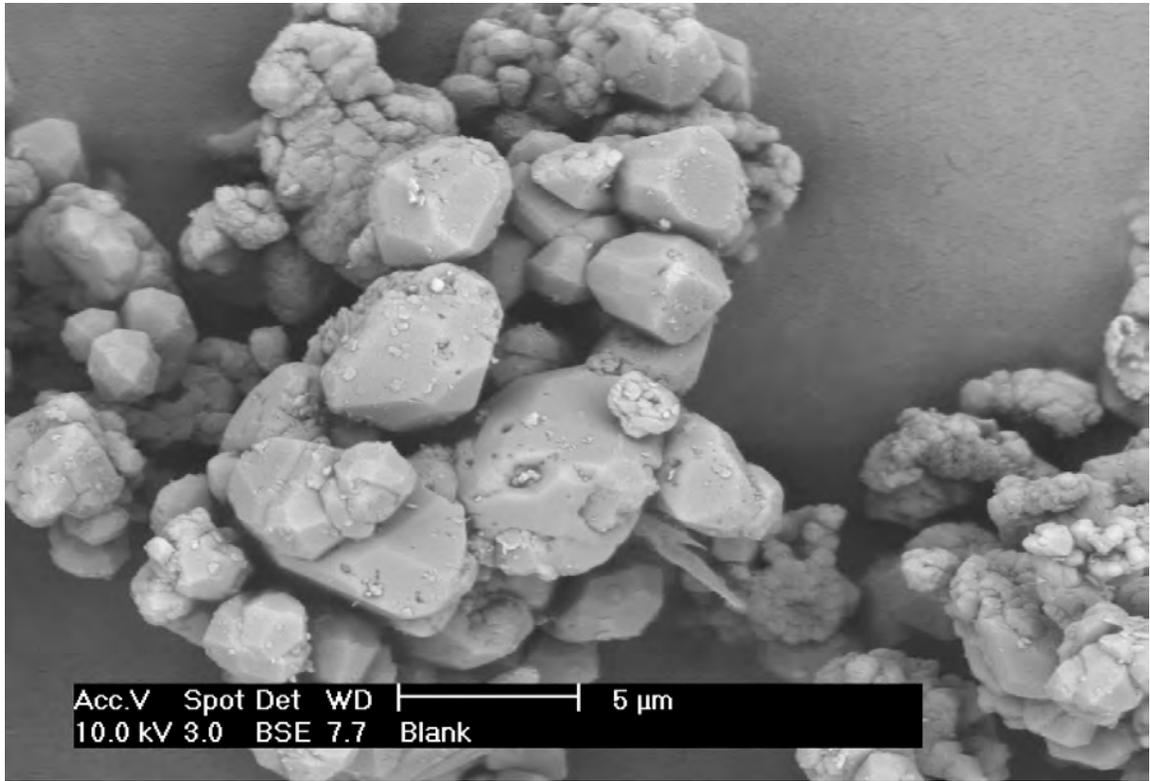


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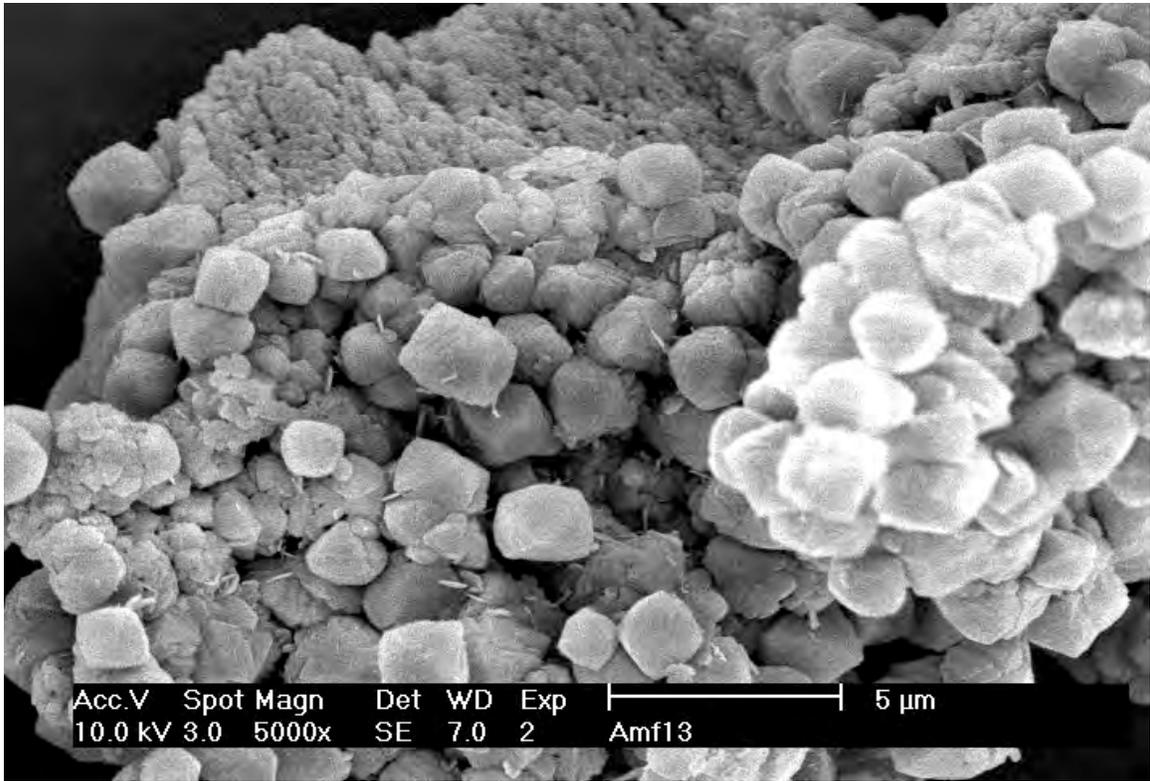


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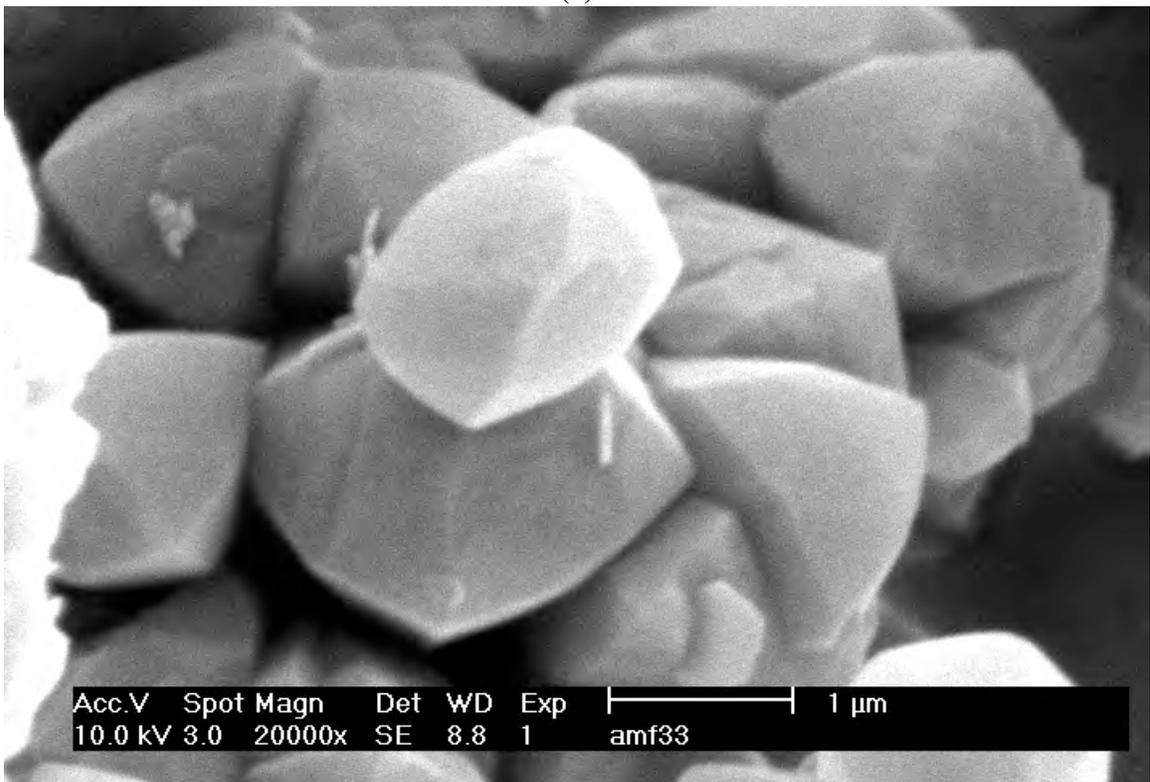
**Figure 1**



**Figure 2**

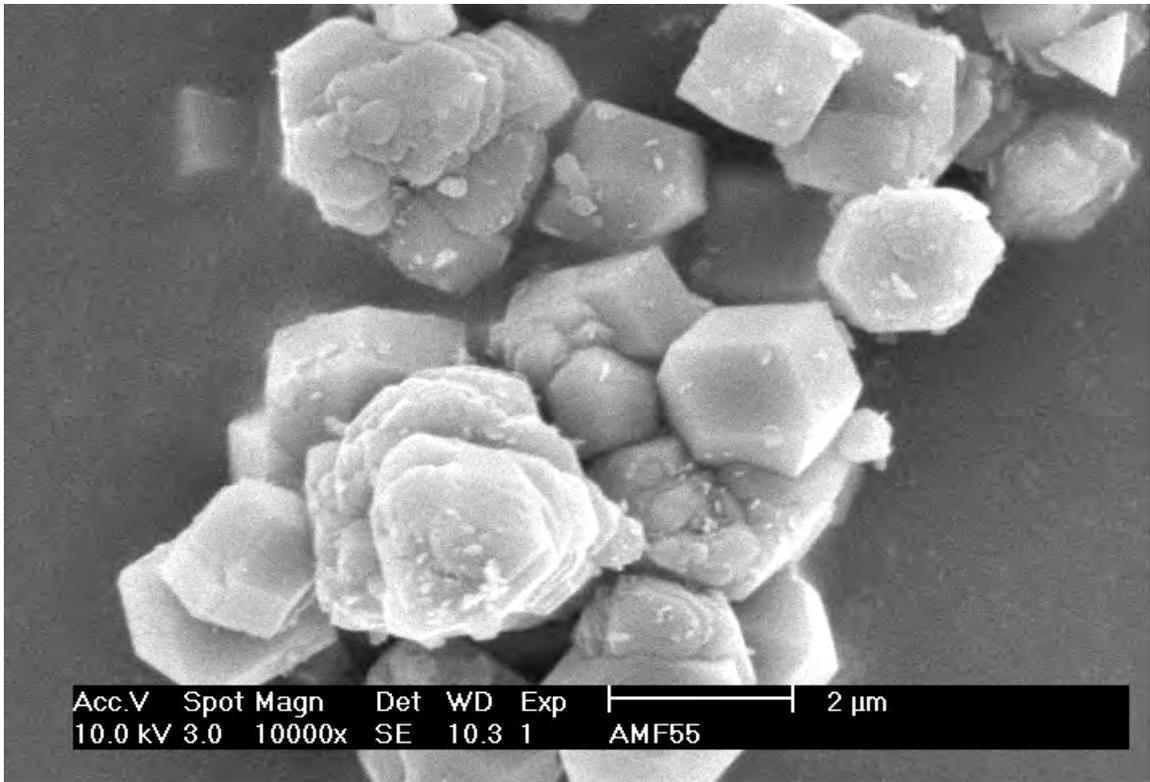


(a)

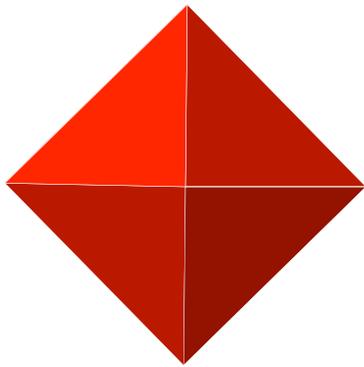


(b)

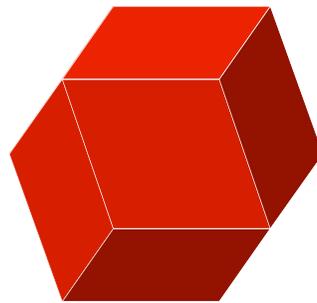
Figure 3



(c)



(d)



(e)

**Figure 3**

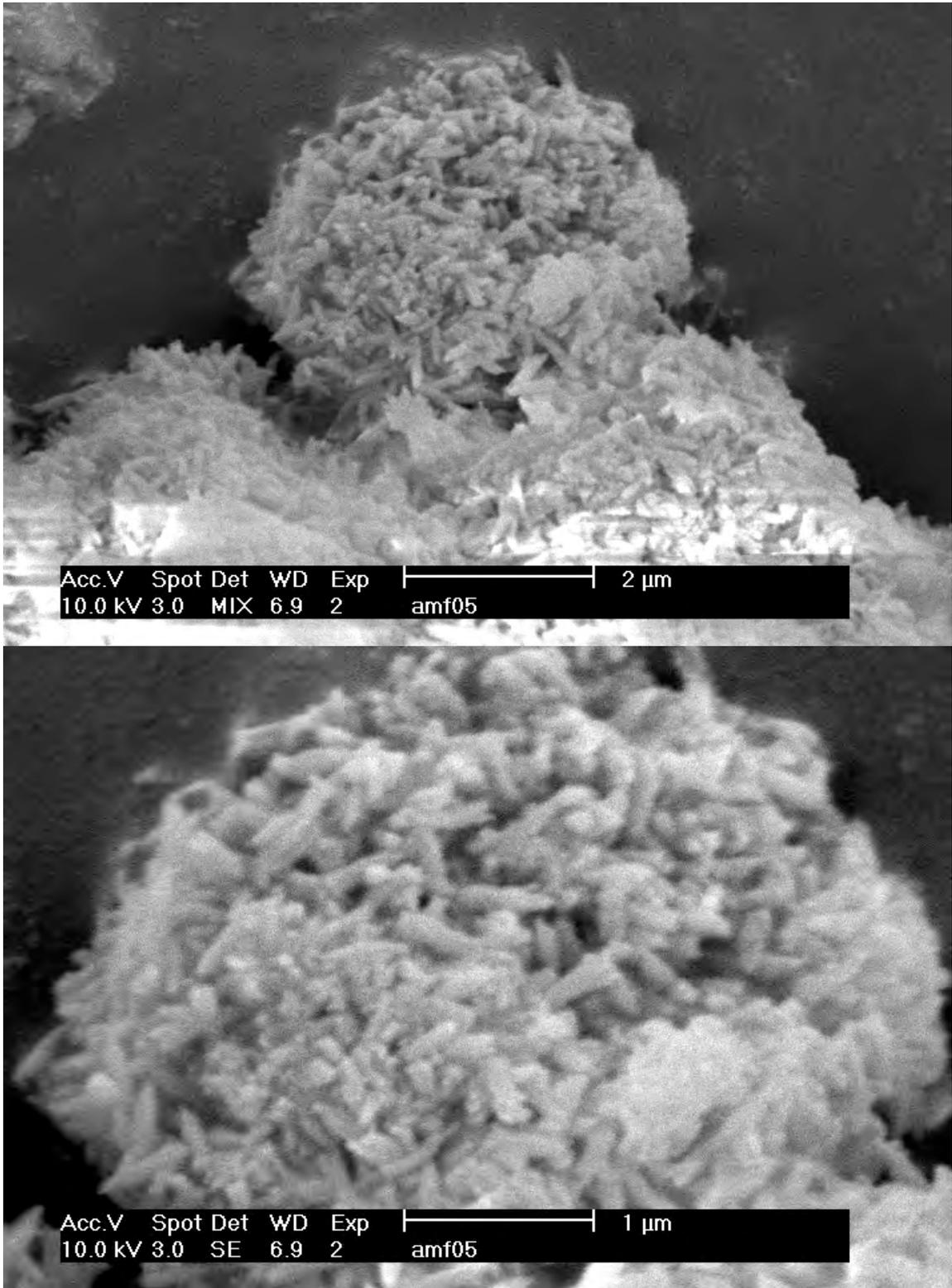
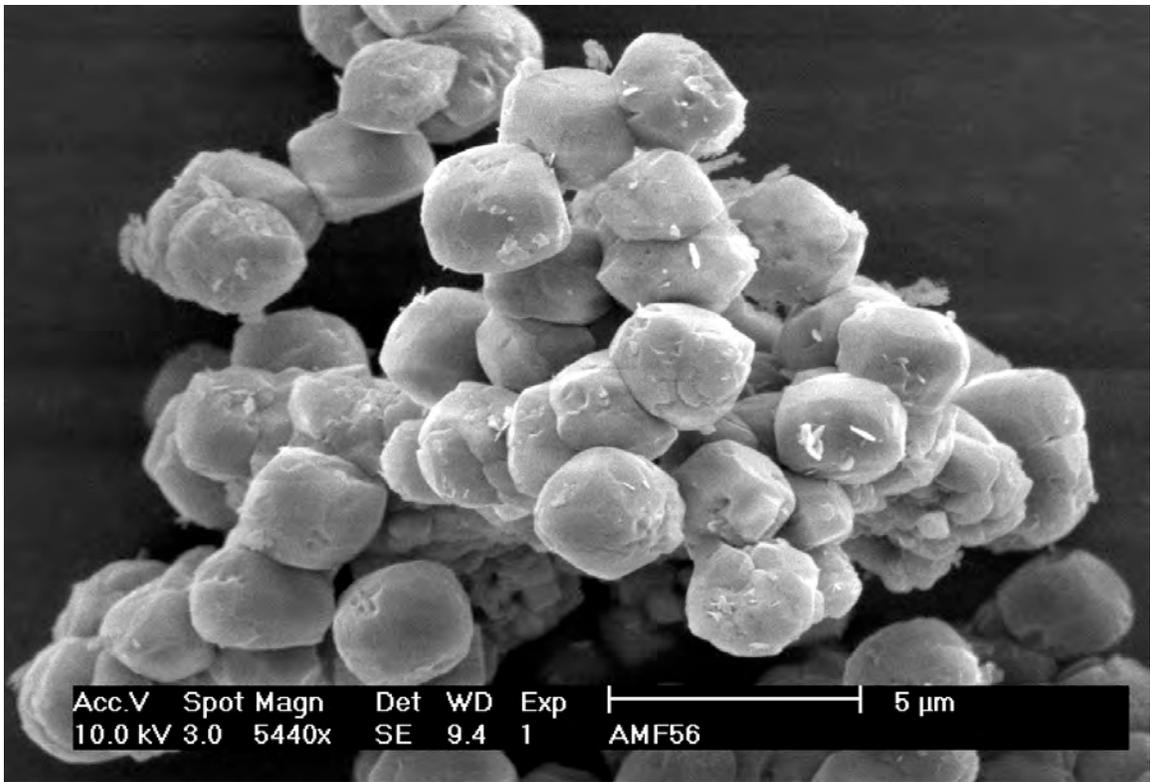
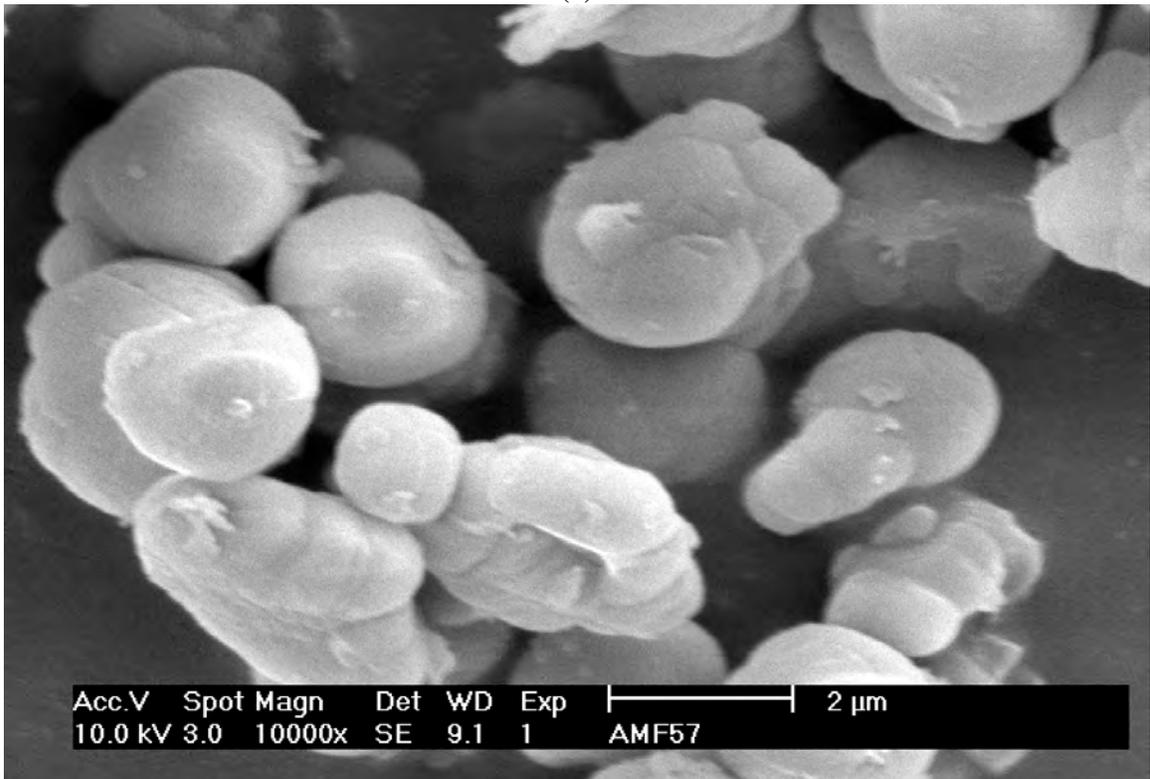


Figure 4

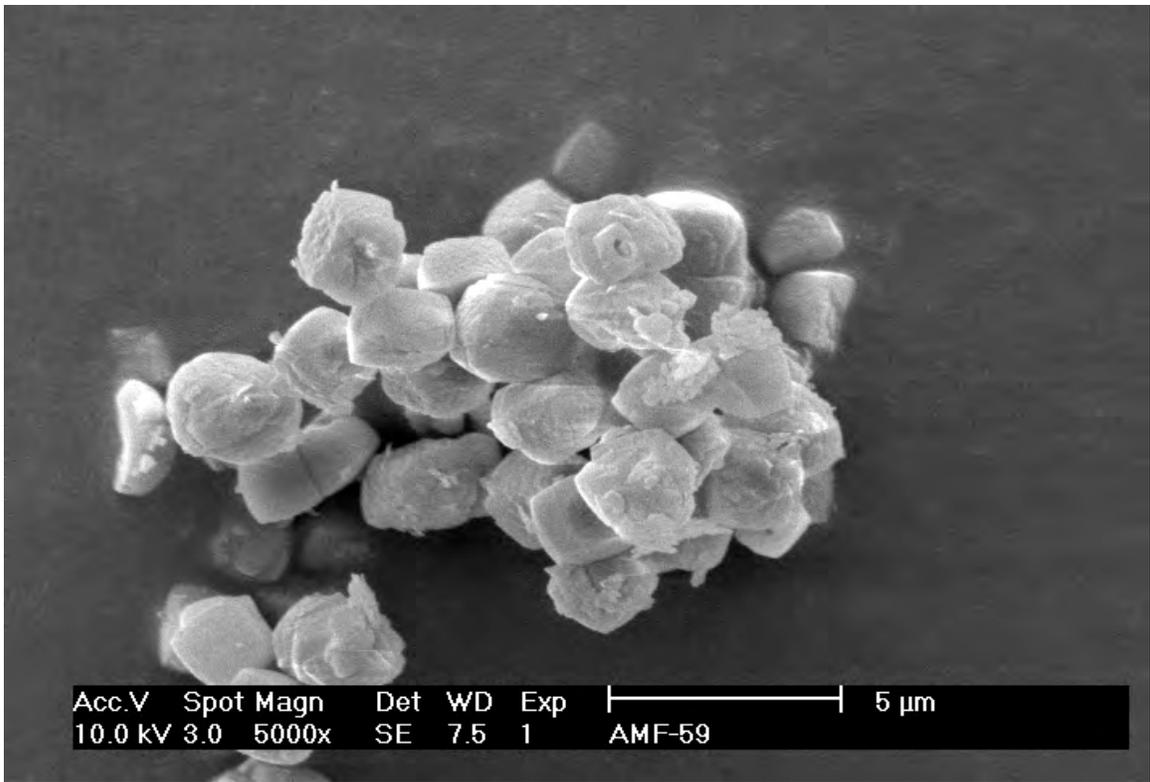


(a)

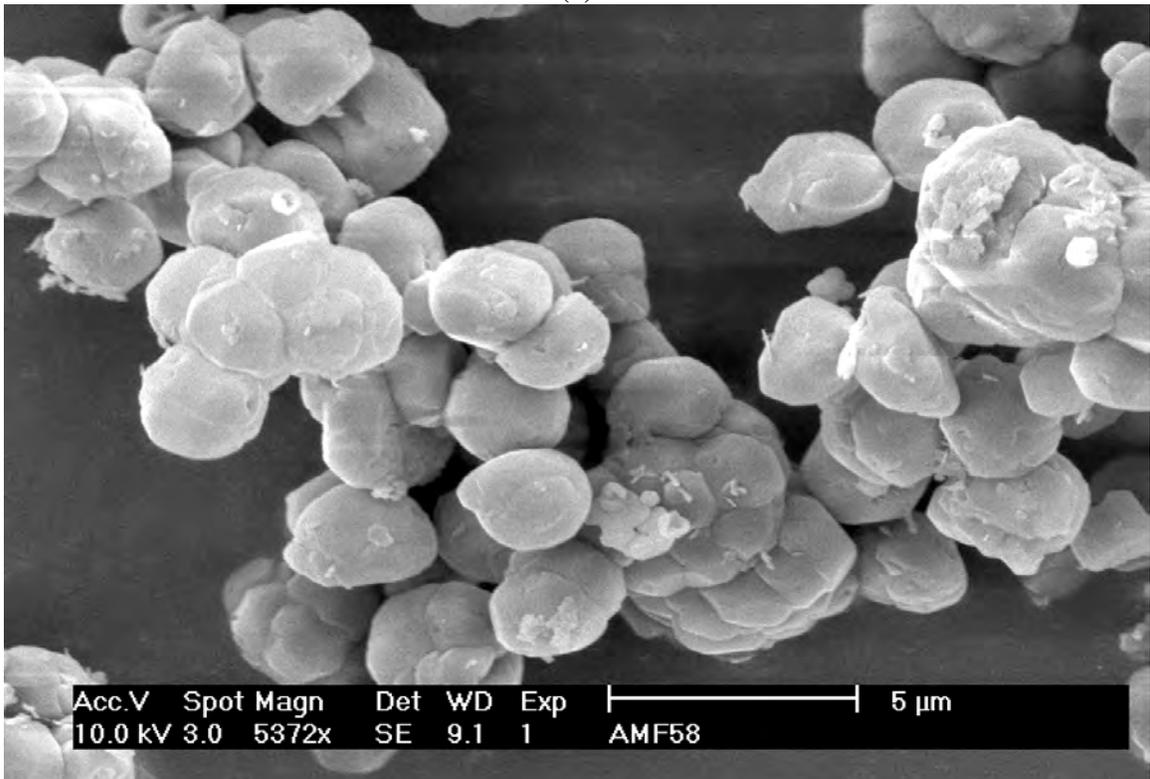


(b)

**Figure 5**



(c)



(d)

**Figure 5**