

## Supplementary Information

### Selective crystallization of D-mannitol polymorphs in water-isopropyl alcohol through swift cooling process

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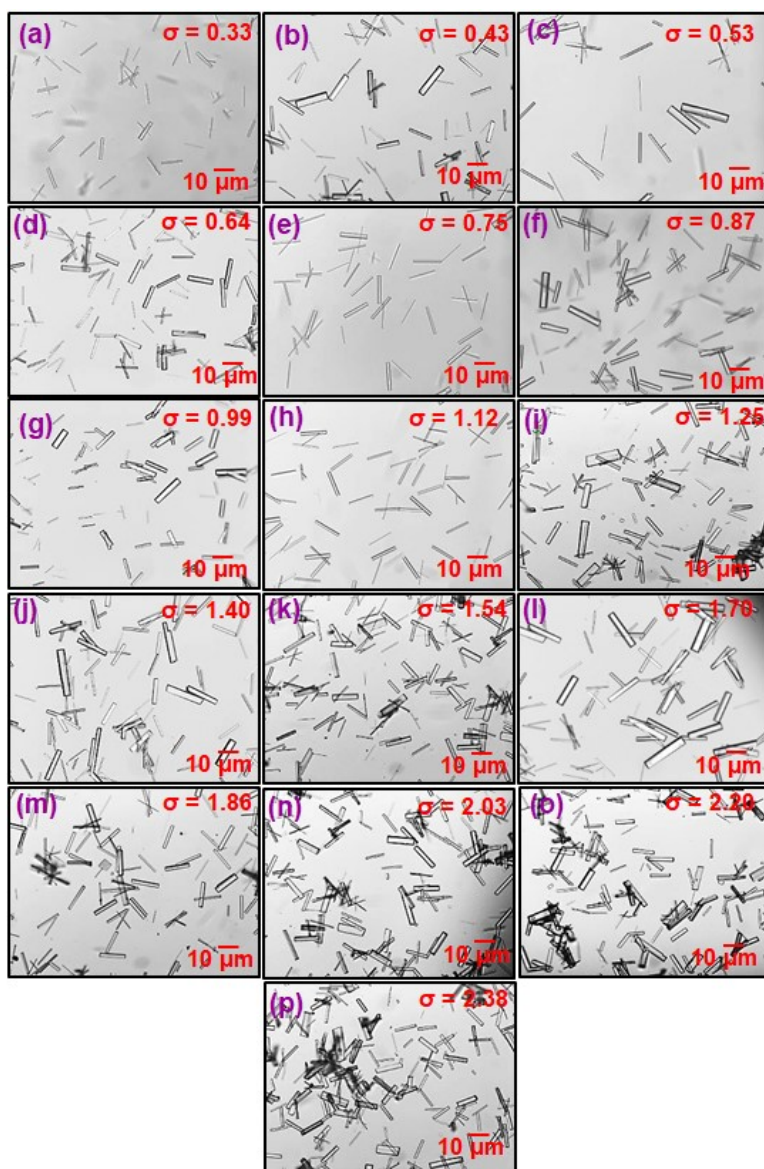


Fig. S1 (a–p) In-situ microscopic images showing nucleation of D-mannitol polymorph at low relative supersaturation  $\sigma = 0.33$ -2.38.

Table S1. Aspect ratio of crystals corresponding to different morphologies

| Morphology              | Aspect Ratio (L/W) |
|-------------------------|--------------------|
| Needle (form I)         | 3                  |
| Thin needle (form II)   | 55.86              |
| Thick needle (form III) | 12.94              |

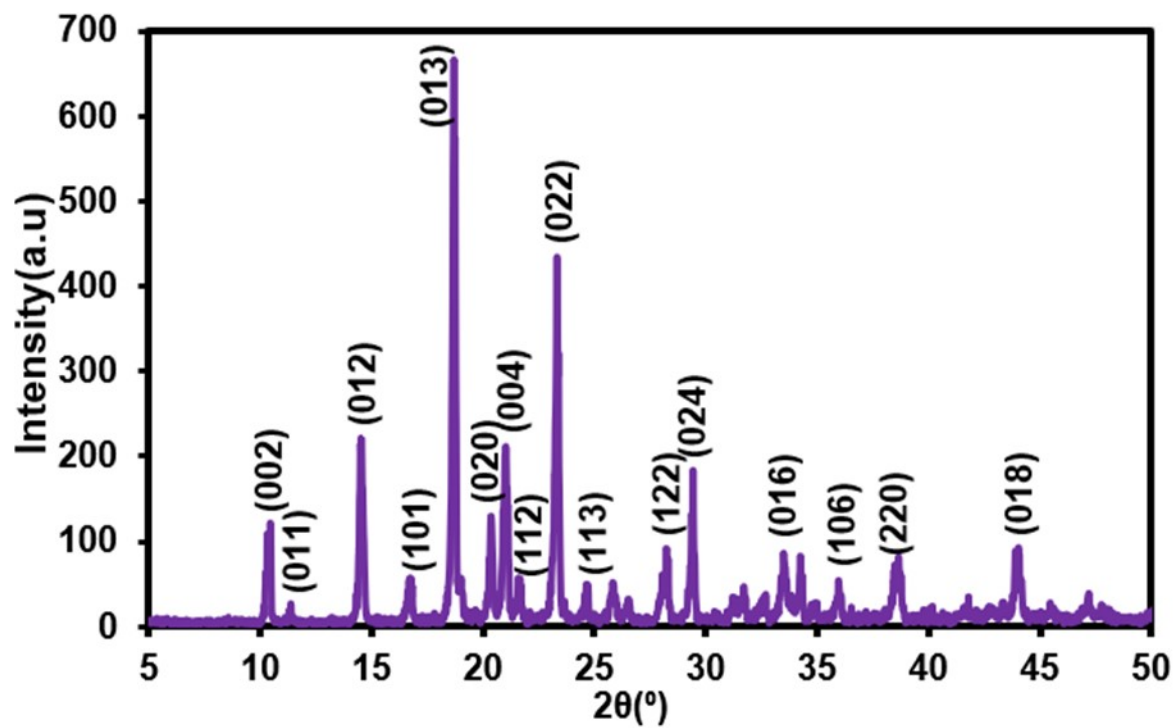


Fig. S2 PXRD pattern of the crystals obtained after the transformation, confirming the formation of form I.

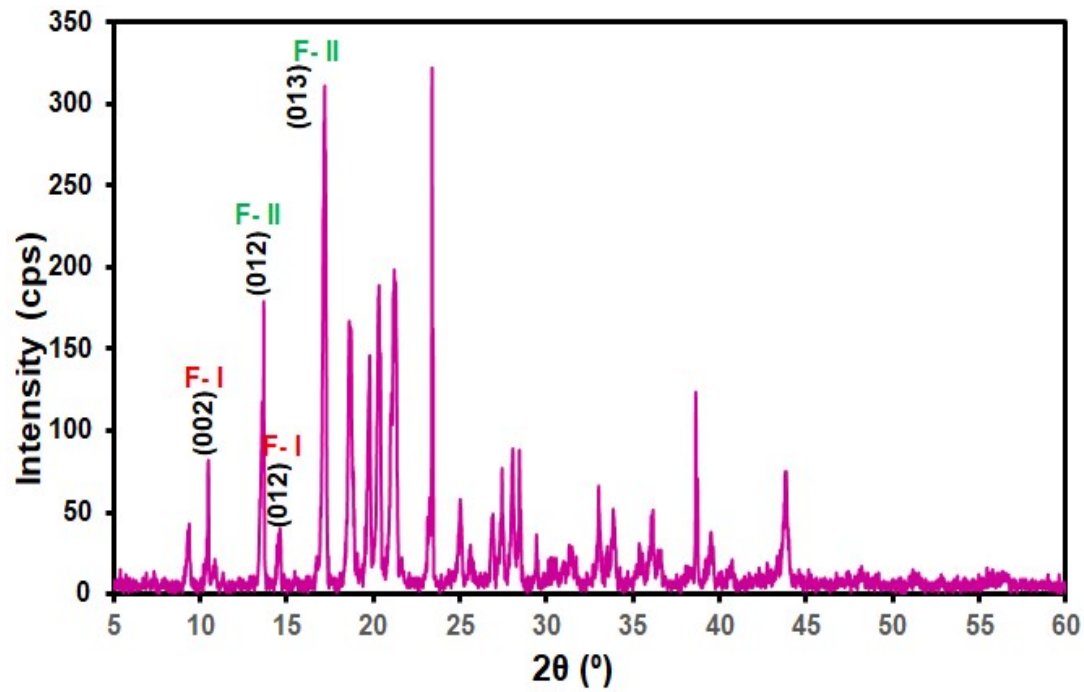


Fig. S3 PXR D pattern of concomitant nucleation of form I and form II polymorph. With the corresponding characteristic peak indicated with hkl of both forms.

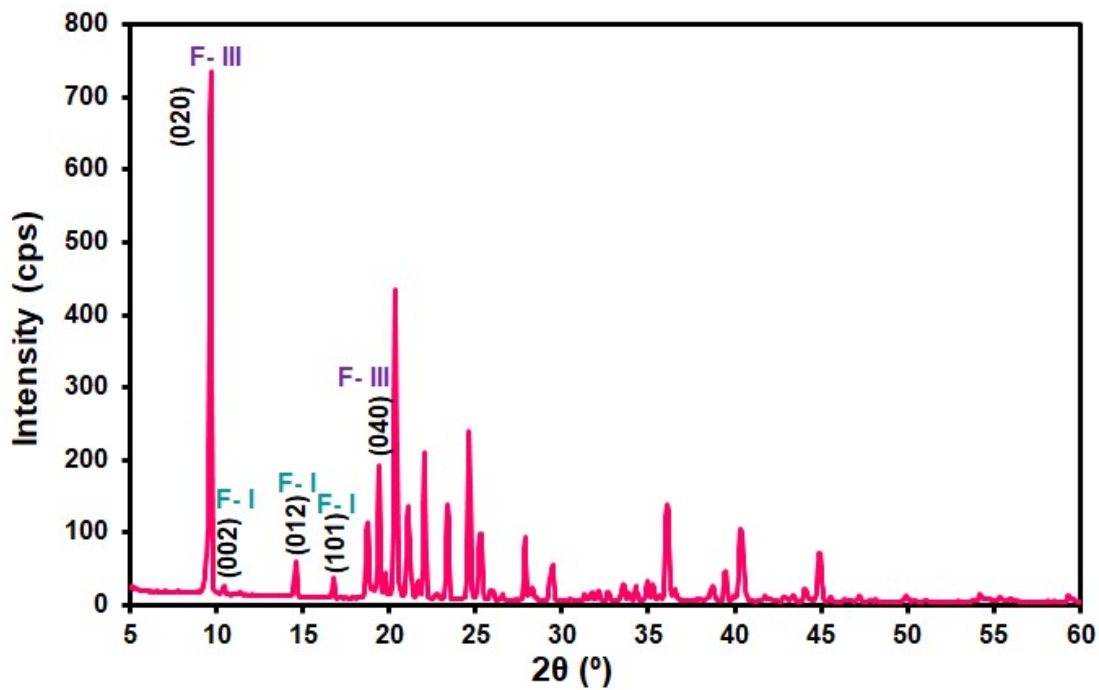


Fig. S4 PXR D pattern of concomitant nucleation of form I and form III polymorph. With the corresponding characteristic peak indicated with hkl of both forms.

Table S2. Lattice parameter values for the polymorphic forms of D-mannitol obtained in this work.

| Lattice<br>parameter     | Form I                            |              | Form II                           |              | Form III                          |              |
|--------------------------|-----------------------------------|--------------|-----------------------------------|--------------|-----------------------------------|--------------|
|                          | Literature<br>value <sup>21</sup> | Present work | Literature<br>value <sup>21</sup> | Present work | Literature<br>value <sup>21</sup> | Present work |
| <b>a (Å)</b>             | 5.538                             | 5.5101(6)    | 4.865                             | 4.8984(5)    | 4.899                             | 4.9122(23)   |
| <b>b (Å)</b>             | 8.580                             | 8.5820(9)    | 8.873                             | 8.9709(10)   | 18.268                            | 18.2682(19)  |
| <b>c (Å)</b>             | 16.795                            | 16.7906(12)  | 18.739                            | 18.7251(17)  | 5.043                             | 5.1166(21)   |
| <b>β (°)</b>             | 90                                | 90           | 90                                | 90           | 118.39                            | 118.40(4)    |
| <b>v (Å<sup>3</sup>)</b> | 798.0                             | 793.98(10)   | 809.0                             | 822.83(10)   | 397.0                             | 403.89(19)   |