Supporting Information (SI)

Formation and Morphology Simulation of CL-20/4,5-MDNI Cocrystal Explosives with Different Proportions in Ethanol/Acetonitrile Binary Solvents

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A.Supplementary note

Note A1: Attachment energy model

The attachment energy (E_{att}) represents the amount of energy released as a growth unit attaches to the surface of a crystal. Its definition formula (1) is as follows:

$$E_{\mathrm{att}} = E_{latt} - E_{slice} \tag{1}$$

In the above expression: E_{latt} represents the total lattice energy of the crystal, in kJ/mol; E_{slice} denotes the energy contained in one growth unit having a thickness of d_{hkl}, in kJ/mol.

In order to fit the crystals grown in the solvent environment, the attachment energy was adjusted to E_{att}^{m}:

$$E_{att}^{m} = E_{att} - E_{s} \tag{2}$$

Among them, the energy correction term E_s is added. The specific definition equation (3) is as follows[1]:

$$E_s = E_{\mathrm{int}} \times \frac{A_{acc}}{A_{box}} \tag{3}$$

In the equation, E_s represents the interaction energy of the solvent with a given crystal plane, in kJ/mol; A_{acc} is the solvent-accessible area of the crystal plane (h k l), in Å²; A_{box} is the area of the crystal plane, in Å²; E_{int} denotes the interaction energy between the crystal plane layer and the solvent layer, with its calculation formula (3) is[2]:

$$E_{\text{int}} = E_{tot} - E_{sur} - E_{sol} \tag{4}$$

In the formula, E_{tot} refers to the overall interaction energy between the solvent layer with the crystal surface layer, kJ/mol; E_{sur} is the energy of the crystal surface layer, kJ/mol; E_{sol} represents the energy of the solvent layer, kJ/mol.

In the MAE model, the adjusted growth rate R_{hkl}^{m} of each crystal plane varies in direct proportion to the absolute magnitude of E_{att}^{m}:

$$R_{hkl}^{m} \propto | E_{att}^{m} | \tag{5}$$

Note A2: PBC theory

In 1980, P. Hartman and P. Bennema introduced the far-reaching theory of periodic bond chains, abbreviated as the PBC model[3]. This theory suggests that in the three-dimensional structure of crystals, there exist continuous bond chains composed of atoms or molecules connected by strong interaction forces. These bond chains also exhibit spatial repetitive symmetry due to the periodic arrangement of atoms or molecules within the crystal. Therefore, it is called a “periodic bond chain”. According to this theory, crystal planes can be classified into three types based on the number of PBC vectors: flat planes (F-plane), stepped planes (S-plane), and twisted planes (K-plane). The F-plane, S-plane, and K-plane correspond to containing two or more PBC vectors, containing one PBC vector, and not containing a PBC vector, respectively. The surface with high mesh density is an important crystal surface, while the surface without PBC vector disappears in the final crystal morphology.

References

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