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Nanoscale 2CL-20·HMX High Explosive Cocrystal by Bead Milling

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ABSTRACT

Energetic nanoscale 2CL-20·HMX, a cocrystal of CL-20 and HMX at a 2:1 molar ratio, was prepared by a novel method of bead milling an aqueous suspension of ε-CL-20 and β-HMX. Conversion of the coformers to the cocrystal form was monitored by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis of specimens sampled at various milling times. Complete conversion to the cocrystal form was achieved by 60 minutes of milling. Rounded 2CL-20·HMX cocrystal particles with a mean size below 200 nm were produced. A mechanism for the conversion of the coformers to the cocrystalline form is postulated based on the experimental results. As an inherently safe manufacturing method, the aqueous bead milling process has a great potential in advancing the cocrystal research and applications in the field of energetic materials.

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Energetic materials are an important category of materials that have wide applications including mining and munitions. As accidental detonations of energetic materials can result in loss of lives and tremendous cost, there is great interest in reducing their initiation sensitivity,[1-5] particularly of those based on more powerful and generally more sensitive high explosives (HEs) including 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20) and 1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX). One of the strategies that is currently pursued to retain the performance of these explosives while significantly reducing their sensitivity is to employ their cocrystals in formulations,[6-9] as cocrystals can have distinct properties compared to the corresponding coformer crystals.

CL-20 was reported to form cocrystals with HE coformers including HMX, 2,4,6-trinitrotoluene (TNT), and 1,3-dinitrobenzene (DNB).[7-9] The cocrystal with HMX at a molar ratio of 2:1 (2CL-20·HMX) is particularly attractive as it has a relatively high density, a good predicted detonation velocity, and an impact sensitivity similar to β-HMX which was attributed to a higher degree of hydrogen bonding in the cocrystal relative to that in HMX and CL-20.[7] Fig. S1 shows the molecular structures of CL-20 and HMX and also the unit cell of 2CL-20·HMX cocrystal.

The 2CL-20·HMX cocrystal was first produced by Bolton et al. by a solution precipitation route[7] and has since been made by solvent drop grinding using resonant acoustic mixing.[10] Solvent drop grinding is a commonly used variation to the solid-state grinding employed in mechanical cocrystal formation,[11] where the addition of a very small amount of solvent can facilitate the conversion to cocrystals.[12] Impurities, typically in the form of coformer crystals, are commonly observed in the final product from these methods. Furthermore, the 2CL-

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20·HMX cocrystal prepared by these techniques often has a relatively large particle size with undesirable plate-like morphology.

The particle size and morphology are important physical characteristics of an HE crystal. Nanoscale HE particles exhibit significantly lowered initiation sensitivity and reduced critical diameter compared to larger particles.[1,13-15] HEs with rounded morphology in plastic bonded explosives were found to produce less sensitive materials.[16-18] Energetic cocrystal with nanoscale particles size and rounded morphology were recently reported.[19, 20] These features have the potential to further improve the physicochemical properties of 2CL-20·HMX cocrystal. However, it is quite challenging to separate nanoscale particles from a gas phase as in the reported methods.[19, 20] The development of a safe and simple manufacturing method for nanoscale 2CL-20·HMX cocrystal is required to advance the understanding of this novel material and assess its potential as a substitute for conventional materials.

In this communication, we report a novel way of producing nanoscale cocrystal of 2CL-20·HMX by bead-milling an aqueous suspension of ε-CL-20 and β-HMX at the stoichiometric ratio of the cocrystal. Temporal analysis of the milling suspension composition was performed to elucidate the transition process from the discrete coformers to the cocrystalline phase during milling. The process is shown to completely convert the precursor materials to the cocrystalline form. This aqueous process offers a safer alternative for preparation of cocrystals of explosive materials.

The aqueous suspension was prepared by adding 22.2 g of ε-CL-20 (ATK Inc.) and 7.5 g of β-HMX (BAE Systems) into 400 mL of de-ionized water. Both HEs have a mean particle size of ~ 1-2 μm. The suspension was then stirred and loaded into a NETZSCH MiniCer bead mill. A general schematic of the bead milling process is shown in fig. S2. The milling was performed at

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6800 RPM using 300 μm yttria-stabilized zirconia beads. During the milling process, specimens were collected at 0, 10, 20, 30, 40, and 60 min for analysis. The collected specimens were analyzed using powder X-ray diffraction (XRD, Rigaku ultima IV XRD system with Cu Kα radiation at λ=1.5418 Å) after being dried on the sample holders at room temperature. Specimens for scanning electron microscope (SEM) imaging were prepared similarly by depositing suspension droplets onto clean silicon wafers (size: 5 mm x 5 mm) and dried at room temperature. The morphology of the particles at different milling times was observed using a field-emission SEM (Auriga CrossBeam Workstation, Carl Zeiss).

XRD patterns of specimens taken from the mill are shown in fig. 1. The results suggest that the material completely converted to the 2CL-20·HMX cocrystal form after 60 min of milling. It can also be observed that the strongest peak of 2CL-20·HMX cocrystal[7] at 13.2^{o} grows in intensity which is accompanied by the decrease of the peak of ε-CL-20 at 13.7^{o}[21] as the milling time increases. The change of the relative intensity clearly demonstrates the progressive conversion to the cocrystalline form.

Fig. 2 shows the morphological evolution of the crystal particles. Most of the coformer crystal particles (fig. 2a) are ~ 1 μm. The mean particle size of the discrete coformers was substantially decreased after 10 min of milling (fig. 2b), with no conversion to the cocrystalline material as suggested by the XRD analysis. Plate-like crystal particles with dimensions less than 500 nm started to appear in the specimen being milled for 20 min, as indicated by the arrow in fig. 2c. The plate-like particles were assigned to the 2CL-20·HMX cocrystal as (1) 2CL-20·HMX cocrystal is known to have plate-like morphology;[7] (2) the appearance of these particles and diffraction peaks from 2CL-20·HMX cocrystal in the XRD pattern occurred at the same time; and (3) more plate-like particles were observed in specimens upon further milling (fig. 2d and

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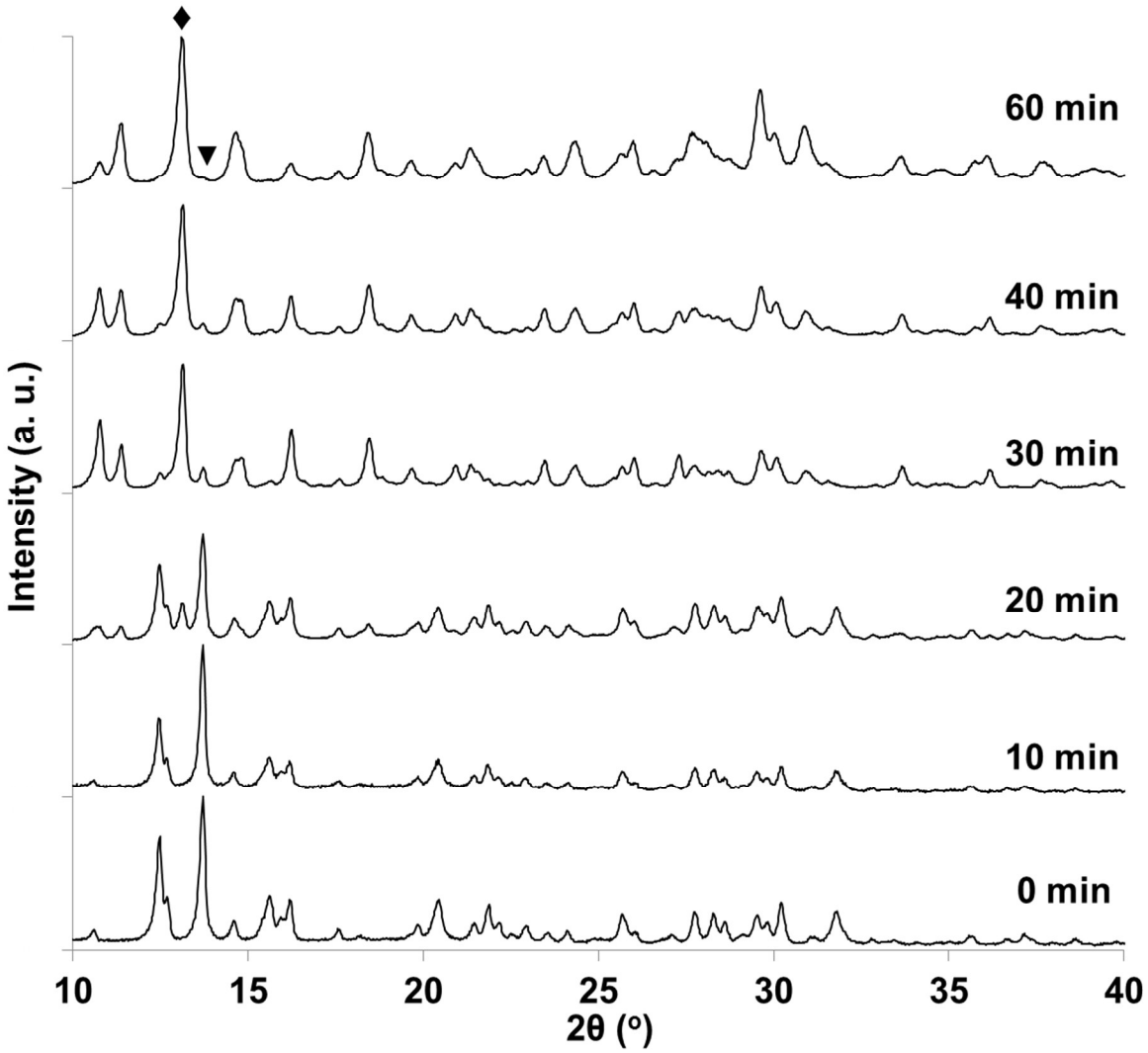

Figure 1. Powder X-ray diffraction (XRD) patterns of CL-20 and HMX (molar ratio 2:1) milled for 0-60 min. The diamond (♦) and triangle (▼) point to the diffraction peaks at 2θ of 13.2° and 13.7° from 2CL-20·HMX cocrystal and ε-CL-20, respectively.

2e, respectively). The observation of these relatively large cocrystal particles seems to be contradicting to the intensive collisions between the grinding media and particles and between the particles themselves occurring during the milling process. It is possible that some growth is occurring during drying of the sampled specimens.

Since both the XRD and SEM analysis show that there is no cocrystal formed after 10 min of milling and the amount of the cocrystalline material rapidly increases between 20 and 30 min, it is likely that nucleation of the cocrystal occurs between 10 and 20 minutes of milling

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followed by a rapid conversion during 20 to 30 minutes. After 60 minutes of milling, the obtained 2CL-20·HMX cocrystal particles have a very small mean particle size (< 200 nm as shown in fig. 2f). Most of the cocrystal particles have a rounded morphology due to the milling, which eliminated sharp edges that are typically observed in solution grown 2CL-20·HMX cocrystal[7] and can lead to higher initiation sensitivity.[16-18]

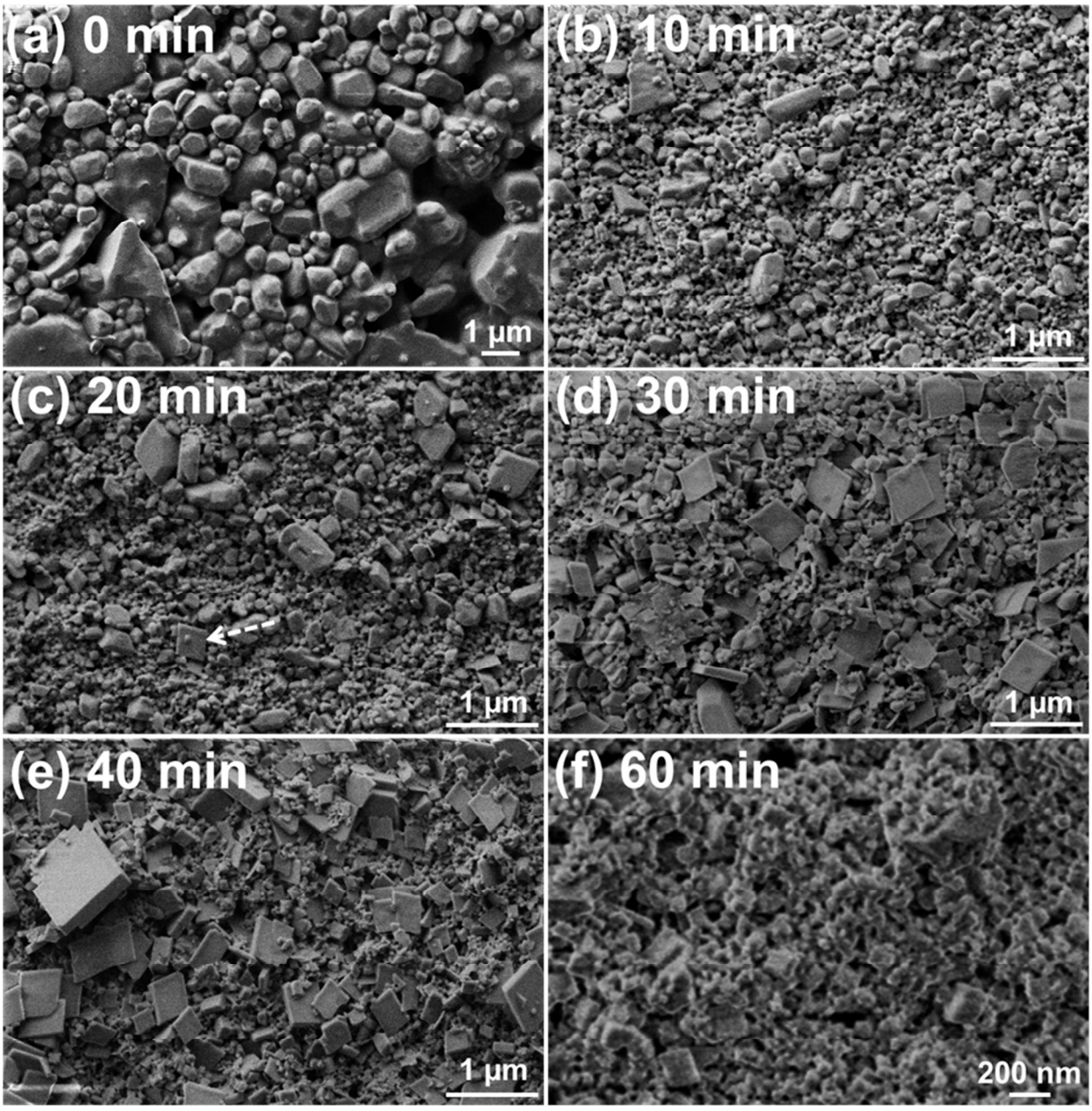

Figure 2. Scanning electron microscope (SEM) images (a-f) of specimens sampled at a milling time of 0-60 min.

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The phase transformation during mechanical processing such as grinding or bead milling can be mediated by the formation of a hydrate, amorphous phase, or liquid phase.[22-24] It is interesting to note that α-CL-20, a hydrate crystal form of ε-CL-20 which forms after extensive bead milling of ε-CL-20,[25] was not observed during the milling of ε-CL-20 and β-HMX mixture. The fact that cocrystal was formed only after significant milling of 10-20 min suggests that amorphization commonly occurred during extensive milling may contribute to the nucleation of the cocrystalline phase. The crystal growth of 2CL-20·HMX cocrystal may have a mechanism resembling that of solution-mediated phase transformation in slurry crystallization.[26] Both ε-CL-20 and β-HMX are known to have low solubility in water. But as the size of crystal particles was reduced, solubility increased during the bead milling process, according to the Kelvin equation.[27] The increased solubility from nanoscale ε-CL-20 and β-HMX possibly assisted the full conversion to cocrystal after milling for about 60 min.

Compared to other processes, production of 2CL-20·HMX cocrystal by bead milling is distinct: (1) The process is shown to completely convert the coformer crystals to the cocrystalline form. This is important as impurities can affect the properties of HEs, especially the sensitivities dramatically. (2) Extremely small cocrystal particles with rounded morphology are attained. These features are expected to reduce the shock sensitivity of the energetic cocrystal. (3) The conversion process takes place in aqueous media and the obtained nanoscale cocrystal particles are in a suspension, which make the aqueous bead milling process inherently safe and uniquely suitable for the production of HE crystals in terms of process safety.

In summary, nanoscale cocrystal of 2CL-20·HMX was prepared by bead-milling an aqueous suspension of ε-CL-20 and β-HMX at the 2:1 stoichiometric ratio. The temporal analysis suggests a progressive conversion to the 2CL-20·HMX cocrystalline form reaching full

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completion by 60 min. Cocrystal particles with a rounded morphology and a very small mean particle size of < 200 nm were produced. The conversion seems to take place by a solvent-mediated phase transformation mechanism. This novel and safe preparation method for nanoscale cocrystal seems to have a great potential in advancing the production and application of energetic cocrystalline materials.

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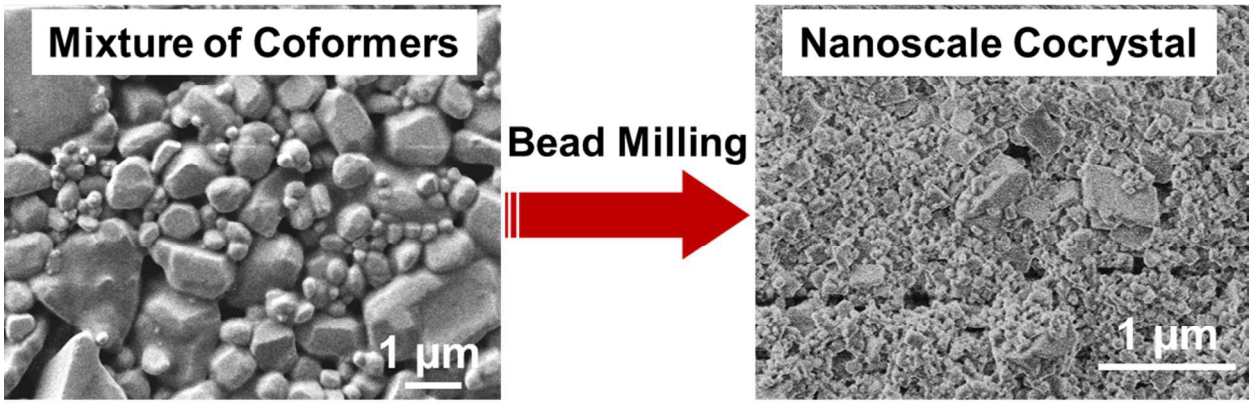
Graphical Abstract:

Nanoscale cocrystal of CL-20 and HMX with rounded morphology was prepared by bead milling an aqueous suspension of the coformers.



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