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Facile Preparation of Self-Sensitized FOX-7 with Uniform Pores by Heat Treatment

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Abstract: Self-sensitized FOX-7 (1,1-diamino-2,2-dinitroethylene) was prepared by a facile heat treatment process near the decomposition temperature. Field emission scanning electron microscopy (FE-SEM) shows the self-sensitized FOX-7 becomes multiple layers and porous after heat treatment. N_2 adsorbance measurements revealed that its specific surface area (6.754 $m^2 g^{-1}$) is 20 times of the area of expanded ammonium nitrate. The SAXS tests further indicate the existence of a large amount of voids in self-sensitized FOX-7 and the pore size is about 30 nm, belonging to mesopore (2.0–50 nm). Based on the analysis of X-ray powder diffraction (XRD), the self-sensitized porous FOX-7 consists of α-phase and a spot of γ-phase. The TG-DSC results show that the self-sensitized FOX-7 exhibits excellent thermal stability. The impact, frication and electrostatic spark sensitivities of self-sensitized FOX-7 also have considerable enhancement. This new method provides a promising route for exploring new green primary explosive replacements.

Keywords: Energetic materials · Porous · Self-sensitized · FOX-7 · Heat treatment

1 Introduction

The primary explosives are a kind of sensitive explosive used in initiating devices like primers and detonators to generate a detonation wave when subjected to impact, fraction, heat, flame or electric spark [1]. Most of the common primaries in actual production, such as lead azide (LA) [2], lead styphnate (LS), dinitrodiazophenol, the coordinate on compound of Cadmium perchlorate and carbohydrazide (GTG), nickel hydrazine nitrate (NHN) etc., are hypertoxic and can cause great harm to the environment and human health [3–5]. It is obligatory to explore green primary explosives. Up to now, great efforts have been made by many research groups to find environmental friendly replacements for the toxic primary explosives [6–8]. Unfortunately, long time has passed, people still did not find the appropriate one, which is sensitive enough, stable enough and has good explosive performance [6].

High explosives are divided into two categories: primary explosives and secondary explosives. Secondary explosives are characterized by their perfect detonation property, such as brisance, power and detonation velocity [9,10]. In addition, many of them, such as FOX-7, TATB and HMX, are more environmental friendly than the traditional primaries [11]. If we devote ourselves to make some modification to them, they will predicatively become promising alternatives to traditional toxic primary explosives.

In an earlier work we have reported the preparation of nano-explosives such as nano-TATB [12] and nano-NTO [13] by solvent/nonsolvent recrystallization to explore their potential applications in slapper detonators [14–16]. However, this approach has great disadvantages. It is too complicated and requires a large amount of solvent [17]. In addition, the agglomeration and growth of nano-particles also have great bad influence on their shock initiation behavior [9,18]. According to the hotspot theory of explosive initiation, pores and defects existing in a condensed-phase explosive can substantially increase its sensitivity to initiation by shock impact [19]. Therefore, finding an easy and effective method to increase the porosity and defect density of condensed-phase high explosives is a promising way to sensitized them and make them good alternatives to traditional primaries.

In this paper, we presented a facile method to sensitize explosives and adopted FOX-7 as an example to try this idea out. According to literature [20], the thermal decomposition process of FOX-7 consists of two obvious stages. In the first stage, the temperature ranging from 190 °C to 245 °C, the thermal decomposition rate was rather slow; in the second stage, the temperature ranging from 260 °C to 290 °C, it underwent violent decomposition. Therefore, we could make use of the thermal decomposition characteris-

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tic of FOX-7, by controlling its decomposition temperature to make it decompose slowly. As the decomposed products moving off as small-molecular gases, an ordered porous structure was formed in the residues. Thus the FOX-7 was sensitized with desirable sensitivity and thermal stability, which is essential for primaries [4]. As expected, the resulting modified FOX-7 is not only thermally stable before the temperature reaching to 265 °C, but exhibits considerable improvement in sensitivity. Therefore, this new method provides a promising route for exploring new green primary explosive replacements.

2 Experiment

2.1 Main Materials

1,1-diamino-2,2-dinitroethylene (FOX-7) received from the China Academy of Engineering Physics was as yellow crystals. *N*,*N*-Dimethyl formamide (DMF, $\geq$99.5 %), was purchased from the J&K Chemicals.

2.2 Preparation of Self-Sensitized FOX-7

In order to purify the raw material FOX-7, FOX-7 (1.0 g) was dissolved in a solution prepared by DMF (20 mL) and distilled water (40.6 mL) at 95 °C. After being cooled down to room temperature, a yellow quadrangular prism solid was formed [21]. The product was filtered and washed with distilled water and dried in a vacuum oven in order to purify the FOX-7.

The purified FOX-7 was heated in the KSL-1100X box furnace at 225 °C for one hour and then the self-sensitized FOX-7 was finally obtained.

2.3 Testing Method

Morphologies of purified FOX-7 and self-sensitized FOX-7 samples were examined by field emission scanning electron microscope (FE-SEM, Ultra55). X-ray powder diffraction (XRD) patterns were collected with a Bruker D8 Advance diffractometer with Cu-K_{α} radiation ($\lambda = 0.15406$ nm). The differential scanning calorimetry/thermogravimetry (DSC/TG) analysis on the FOX-7 samples were carried out by a simultaneous thermal analyzer (SDTQ 600) from room temperature to 400 °C in a nitrogen flow of 20 mL min^{-1} at a heating rate of 10 °C min^{-1}. The specific surface area and pore structure of self-sensitized FOX-7 sample were tested with a NOVA 3000 specific surface area instrument. More detailed information of the nanostructure was got by the small-angle X-ray scattering (SAXS) at the SAXS station (BL16B1) in Shanghai Synchrotron Radiation Facility (SSRF), China. The X-ray wavelength was 0.1239 nm and the distance between the detector and the sample was 2075 mm.

The impact sensitivity tests were carried out with a WL-1 type impact sensitivity apparatus. A total of 25 samples of purified FOX-7 or self-sensitized FOX-7 powder per sample (50 mg), were kept between two hardened anvils and hit by a drop hammer of 10 kg from a fixed height (25 cm) by turns. The results were reported in terms of probability of explosion (%). The friction sensitivity experiments were measured with a WM-1 type friction sensitivity instrument consisting of hydraulic system, a pendulum and a pair of sliding columns. The samples were kept between the sliding columns and the relative movement of them created friction, making the samples exploded. The test conditions are: relative pressure: 4 MPa; sample mass: 30 mg; pendulum weight: 1.5 kg; pendulum angle: 90°. Twenty-five experiments were conducted to give a probability of explosion (%). The electrostatic spark sensitivity experiments were tested by a JGY-50 type electrostatic sensitivity apparatus.

3 Results and Discussion

3.1 Morphology of Self-Sensitized FOX-7

Field emission scanning electron microscopy (FE-SEM) images reveal the crystal shape and surface morphology of the purified FOX-7 and the self-sensitized FOX-7. Figure 1

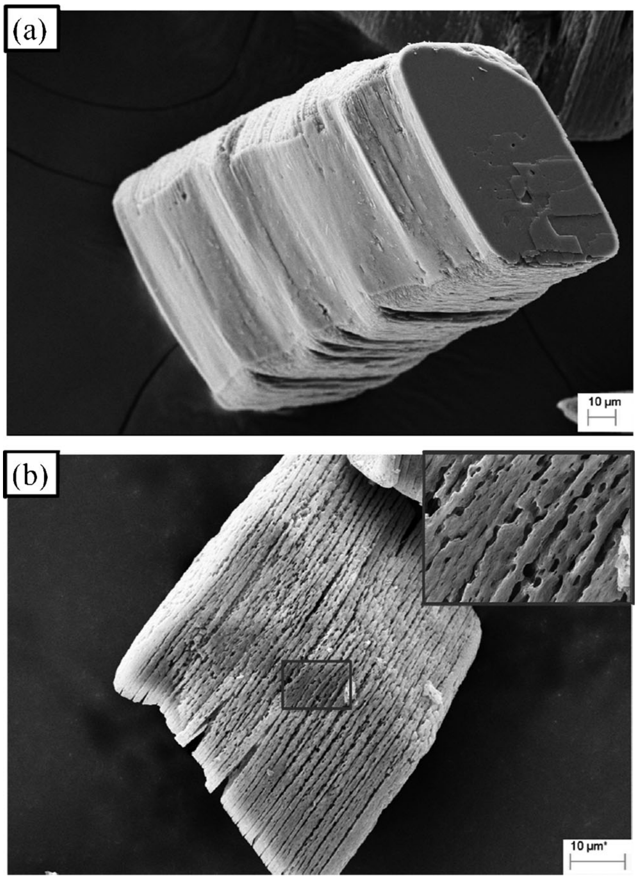

Figure 1. FE-SEM pictures of purified FOX-7 (a) and self-sensitized FOX-7 (b).

(a) and (b) are the FE-SEM images of the purified FOX-7 and self-sensitized FOX-7 after heat treatment, respectively.

Figure 1 (a) shows the purified FOX-7 exhibits a prismatic shape and a compact structure with a much smoother surface than that of the self-sensitized FOX-7. The prismatic FOX-7 is formed by a kind of laminar ordered structure because of oriented growth in the recrystallization process. However, Figure 1 (b) shows that self- sensitized FOX-7 after heat treatment has a loose structure. It has become multiple layers and porous. So, it was also called porous FOX-7. The possible reason assigned for the formation of the loose structure of the multiple layers and porous FOX-7 crystal is that NO_2 is the most active and sensitive group in a explosive molecule, the initial step of FOX-7 decomposition when heated is a nitro-to-nitrite rearrangement, followed by the elimination of NO molecule, [22] which leads to the growth of thousands of pores and holes.

Hot-spot models of initiation and detonation show that voids or porosity ranging from nanometer to micrometer in size within highly insensitive energetic materials have great effect on their sensitivity. According to the hotspot theory of explosive initiation, those pores and holes in the loose structure of FOX-7, suffering from an adiabatic compression when a shock wave arrives, can easily become the initiation hotpots, as a result of which, the porous FOX-7 becomes more sensitive.

3.2 X-ray Diffraction Analysis

FOX-7 is a polymorphic substance and three phases [23] or four phases [24] have been reported in literature. The solid to solid phase transitions prior to chemical decomposition when temperature is increased from the room temperature to 300 °C or above. The initial phase at room temperature is identified as α-FOX-7 whose molecular packing consists of wave-shaped layers with extensive intermolecular hydrogen bonding within the layers and ordinary van der Waals interactions between the layers as described by Bemm and Östmark in 1998 [25]. The phase appearing after the first transition at around 110 °C is defined as β-FOX-7 and this phase transition is completely reversible [26]. When the temperature rises to 160–170 °C, a new phase called γ-FOX-7 appears. On cooling of γ-FOX-7, only $\gamma \rightarrow \alpha$ (below 75 °C) and no transition of the β-phase occurs [23], which is regarded as incomplete since the β-phase transition progress requires a very long time.

Figure 2 shows the XRD patterns of the purified FOX-7 and self-sensitized FOX-7. The XRD patterns indicate that the peaks of self-sensitized FOX-7 have nearly the same diffraction angles as those of the purified FOX-7, implying that self-sensitized FOX-7 is almost of the same crystal structure as the purified FOX-7. The location of $2\theta = 28^\circ$ diffraction peak is completely unchanged and its intensity is always the strongest. However, we can also see from the Figure 2 that the diffraction peak at $2\theta = 27^\circ$ of the purified FOX-7 is much stronger than that of the self-sensitized FOX-7. That is because of the preferable growth of crystal face (0 2 0), which has also been embodied in the FE-SEM picture of purified FOX-7 (Figure 1 (a)). The preferred orientation of purified FOX-7 crystal disappeared after heat treatment, so the diffraction peak at $2\theta = 27^\circ$ becomes less sharp and strong. Moreover, compared with the XRD pattern of purified FOX-7, there is an extra diffraction peak at $2\theta = 22^\circ$, in the pattern of self-sensitized FOX-7, which is attributed to the diffraction peak of γ-FOX-7 [26]. That is because α-FOX-7 transformed into γ-FOX-7 with the temperature rise, but it was an irreversible process since γ-FOX-7 could not transform back into α-FOX-7 completely in the limited time although the temperature cooled down to room temperature finally. Therefore, self-sensitized FOX-7 is actually a kind of mixture of α-FOX-7 and a small amount of γ-FOX-7.

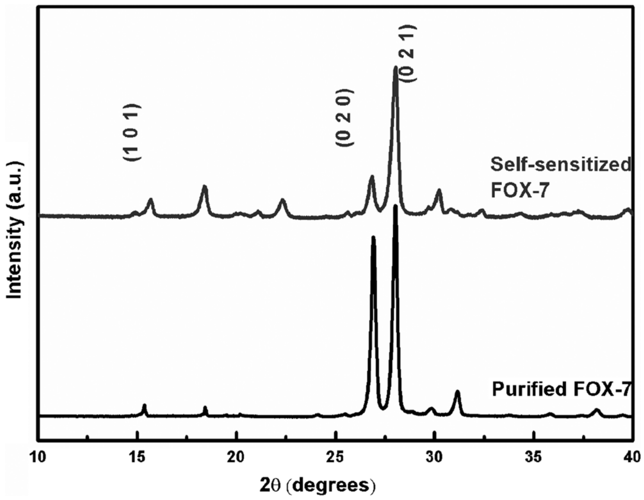

Figure 2. XRD of purified FOX-7 and self-sensitized FOX-7.

3.3 Pore Structure Analysis

Abundant cavities existing in the self-sensitized FOX-7 crystal are of great importance for its self-sensitization, so it is essential to study the pore structures, including specific surface area, pore volume and pore distribution etc. N_2 adsorption method is used to further quantitatively elucidate the multilayer porous structure of the self-sensitized FOX-7 after heat treatment.

The adsorption-desorption isotherm curve, as is shown in Figure 3, was obtained by NOVA3000 to determine the specific surface area and pore size of self-sensitized porous FOX-7. The adsorption amount increases gradually at the low relative pressure (p/p_0), demonstrating the N_2 molecules were adsorbed to the inner surface of the mesoporous from monolayer to multilayer. As shown, the adsorption amount does not reach a plateau near high relative pressure (p/p_0) of 1.0 and the type H3 hysteresis loop is observed according to Brunnauer-Deming-Deming-Teller (BDDT) classification with aggregates of plate-like particles

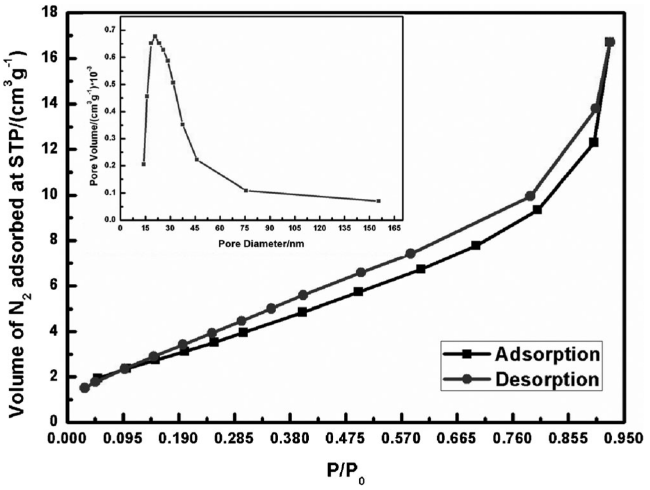

Figure 3. Nitrogen adsorption-desorption isotherm and BJH open pore size distribution plot of self-sensitized FOX-7.

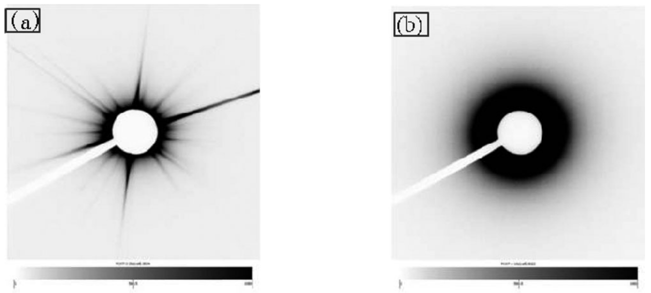

Figure 4. Two-dimensional SAXS patterns of (a) purified FOX-7 and (b) self-sensitized FOX-7.

giving rise to slit-shaped pores [27], which is in good agreement with the observation from FE-SEM images. The BET surface area of self-sensitized porous FOX-7 is 6.754 $m^2 g^{-1}$ measured using multipoint BET method within the relative pressure (p/p_0) range from 0.05 to 0.35 and it is more than twenty times the size of expanded ammonium nitrate explosive (0.3328 $m^2 g^{-1}$) [28]. The Barrett-Joyner-Halenda (BJH) open pore size distribution curve obtained is embedded in Figure 3. From the distribution curve, we know the sample has a narrow open pore size distribution in the range of 2.0–5.0 nm, which can be classified as mesopores (2.0–50 nm). Subjected to the test principle, the N_2 adsorption method can only give the size of open pores. Further research should be made by other test methods.

In order to get more detailed and convictive information of the nanostructure, SAXS was then employed as a more powerful research tool. The two-dimensional SAXS patterns of (a) purified FOX-7 and (b) self-sensitized FOX-7 are shown in Figure 4. Figure 5 provides the log*I*-log*q* curves converted from Figure 4. In consideration of the FE-SEM results in Figure 1, we attempt to adopt the prismatic microvoid as the simulation model to explain the SAXS data.

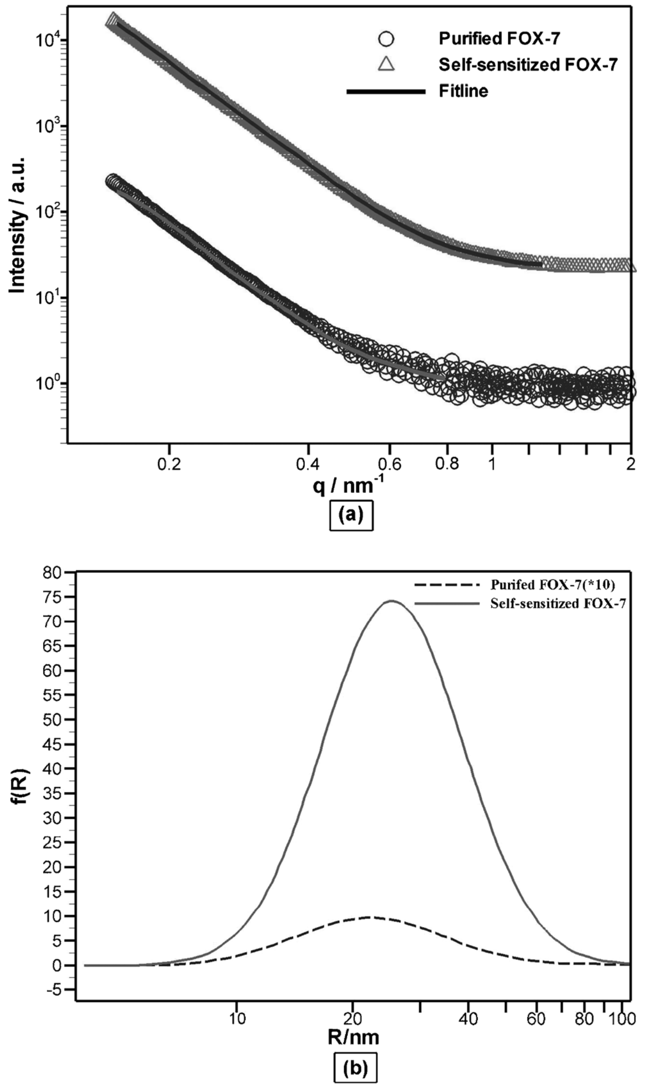

Figure 5. (a) SAXS data and (b) log-normal distribution of pores in purified FOX-7 and self-sensitized FOX-7. Solid lines in (a) represent the fitted results.

From Figure 4 it is obvious that purified FOX-7 shows strong anisotropic scattering, however, after heat treatment the self-sensitized FOX-7 shows strong isotropic scattering. Combined with XRD analysis, we think the strong anisotropic scattering can be explained by the preferred orientation growth of purified FOX-7 crystal as is shown in Figure 2. The heat treatment process enforced the preferred orientation growth and anisotropic scattering disappear at the same time.

In Figure 5 (a), the scattering intensity of self-sensitized FOX-7, compared with that of purified FOX-7, increased significantly, which reveals the existence of a large amount of defects [29,30] and is consistent with the conclusion in SEM characterization (Figure 1). Figure 5 (b) shows the *f*(*R*) of the pores in FOX-7 samples obtained by model fitting. The distribution of self-sensitized FOX-7 slightly shifts toward

Table 1. The fitted results of internal pores in purified and self-sensitized FOX-7.

Samples	Average diameter D [nm]	Void volume
Purified FOX-7	30	25.93
Self-sensitized FOX-7	30.3	2168.80

larger median pore size compared with that of the purified FOX-7, but both distributions mainly focus on the range of 10–60 nm. The fitted results are listed in Table 1. The results show that the average diameter of pores in FOX-7 samples is 30 nm and they undoubtedly belong to mesopores. The voids volume of self-sensitized FOX-7 is 83.6 times that of purified FOX-7, further illuminating the high defect density in self-sensitized FOX-7.

3.4 Thermal Properties (TG-DSC)

The thermal properties of the purified FOX-7 and self-sensitized FOX-7 were investigated using the differential scanning calorimetry/thermogravimetry (DSC/TG) simultaneous thermal analyzer. Figure 6 (a) and (b) shows the thermal analysis results. Figure 6 (a) shows one endothermic peak and two exothermic peaks appear in the purified FOX-7. The endothermic peak occurs around 105 °C, assigned to the $\alpha \rightarrow \beta$ phase transition according to the physical properties of FOX-7 [31]. One of the exothermic peaks occurs at about 202 °C and it can be elucidated by the fact that the rearrangement of nitro-to-nitrite in the molecule leads to the destruction of conjugated system and breakage of hydrogen bonds. Martin Civiš et al. [22] has given a detailed report about the thermal decomposition of FOX-7 and pointed out that the initial step is nitro-to-nitrite rearrangement with the emission of nitrogen monoxide (NO). As shown in Figure 6 (a), this NO emission stage starts from about 185 °C and reaches its maximum decomposition rate around 202 °C, with a mass loss of 20 %, which is consistent with the theoretical value 20.27 %. The mass loss and heat release processes are very slow and gentle. Another exothermic peak occurs at around 284 °C and it is difficult to pinpoint the end of the first exothermic peak and the origin of the second exothermic peak since they connect together, which is, according to Ref. [32], caused by the nonuniform particle size of FOX-7.

However, Figure 6 (b) shows that only one single exothermic peak ($T_p = 287.7$ °C) appears in DSC curve of self-sensitized FOX-7 and the first one at a relative low temperature is hardly observed. That may be explained by the fact that the self-sensitized porous FOX-7 with higher surface area can disperse the accumulated heat effects effectively and therefore the first decomposition cannot occur [33]. It should be noted that the decomposition process of self-sensitized FOX-7 is focused in a narrow temperature range (265–300 °C) compared with that of purified FOX-7 (185–315 °C). This conclusion can also be confirmed by the TG

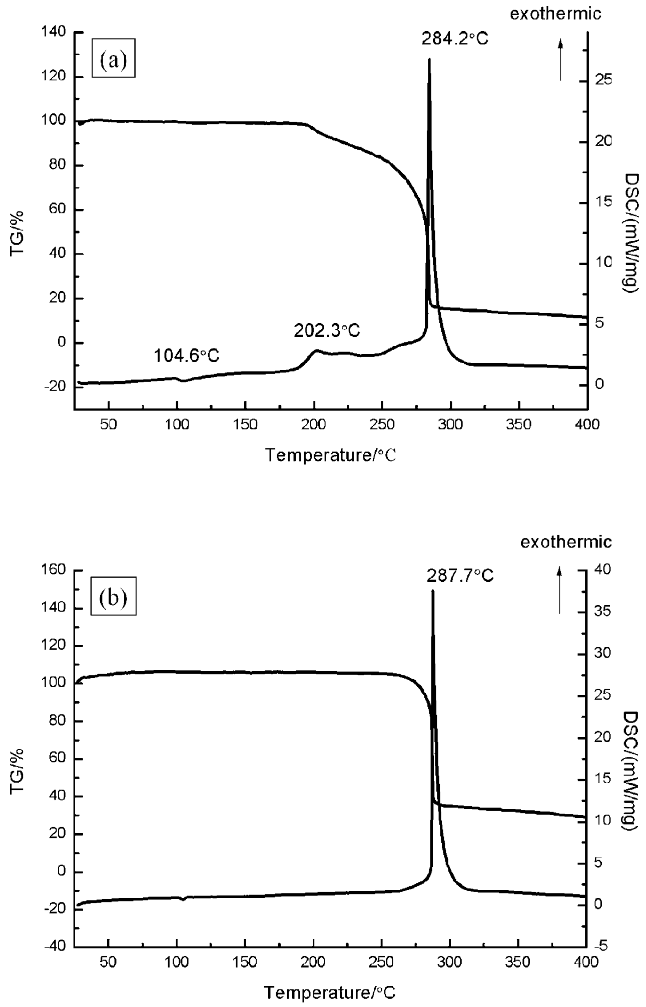

Figure 6. TG-DSC of (a) purified FOX-7 and (b) self-sensitized FOX-7.

curve in Figure 6 (a) and (b). The TG curve of purified FOX-7 displays two obvious mass loss steps over a wide range of temperature, while that of the self-sensitized FOX-7 shows only one drop-off. The DSC and TG results demonstrated that the self-sensitized FOX-7 not only exhibits excellent thermal stability, but also possesses higher energy release efficiency and improved thermal decomposition property.

3.5 Initiation Sensitivity

Sensitivity, response to accidental stimuli [34], is one of the most important explosive properties of energetic material. Considerable attention has been paid to the sensitivity study of self-sensitized FOX-7. As is known, FOX-7 possesses high energy, but it is more insensitive than RDX [35]. However, when pores and holes are introduced into FOX-7 crystal, forming a porous structure, its detonating initiation sensitivity will be improved significantly. The results of

Table 2. The sensitivities of purified FOX-7 and self-sensitized FOX-7.

Sensitivity	Purified FOX-7	Self-sensitized FOX-7
Impact sensitivity	8%	50%
Friction sensitivity	12%	52%
Electrostatic V_{50} [kV]	13.13	8.27
Spark sensitivity E_{50} [J]	2.642	1.030

small-scale impact and frication sensitivity testing were summarized in Table 2.

From the Table 2, it can be seen that the impact and friction sensitivity of self-sensitized FOX-7 are 52% and 50%, respectively. Though the mechanic sensitivities of self-sensitized FOX-7 are still smaller than traditional primaries [36,37], they have considerably increased compared with those of purified FOX-7. It also shows some improvement in electrostatic spark sensitivity: $V_{50}=8.27$ kV, $E_{50}=1.03$ kV, the values are much less than those of the purified FOX-7. It means that this heat treatment method is able to modify the sensitivity of secondary explosives.

It is believed that the improved sensitivity of self-sensitized FOX-7 is closely related to the microstructure of the crystal. The flaws or inhomogeneity existing in the self-sensitized FOX-7 crystal are compressed adiabatically and rapidly by mechanical action, creating a high temperature reservoir of gas. It will subsequently heat the adjacent explosive surface to the auto ignition temperature and thermal decomposition happens, releasing a large amount of heat at the same time, which accelerates the decomposition rate in turn. This process explains how the hot spots form and stimulate the explosion of porous explosive materials.

4 Conclusion

Self-sensitized porous FOX-7 was prepared via a facile heat treatment method. After heat treatment, the self-sensitized FOX-7 became multiple layers and porous with a large amount of mesopores existing in the crystal. Compared with purified FOX-7, the self-sensitized FOX-7 embodied considerable improvements in impact, frication and electrostatic spark sensitivities as well as the thermal stability. This method of sensitizing explosives is feasible and effective. More experiments are essential to further improve the sensitivity and explore the forming mechanisms of the porous structure.

Acknowledgments

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