Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Facile fabrication of Porous CL-20 for Low Sensitivity High Explosives – ESI

Jinpeng Shen, [a,c] Weimei Shi,[a,c] Jun Wang,[a] Bin Gao,[b] Zhiqiang Qiao,[a] Hui Huang,[a] Fude Nie,[a] Rui Li, [a,c] Zhaoqian Li,[b] Yu Liu,[a] and Guangcheng Yang,[*a,c]

[a] Institute of Chemical Materials, China Academy of Engineering Physics, Mianyang 621900, Sichuan, China. E-mail: ygcheng@caep.cn; sjp0388@163.com; Tel: +86-08162544436; Fax: +86-08162544426

[b] State Key Laboratory Cultivation Base for Nonmetal Composites and Functional Materials, Southwest University of Science and Technology, Mianyang 621010, P. R. China

[c] Sichuan New Material Research Center, Mianyang 621000, Sichuan, China

Materials and Sample Preparation

Attention or Caution: CL-20 is a highly dangerous explosive. Unexpected misoperation was discouraged during this work. Proper safety practices and equipment must be used to prevent explosion caused by friction, heat, static shock, or impact. Be aware that the potential for severe injury exists if these materials are improperly handled.

CL-20 was supplied by the Institute of Chemical Materials, Chinese Academy of Engineering Physics with a purity of 99.7 wt%. DMAc and distilled water were used as solvent and non-solvent, respectively. First, the CL-20/β-CD composites were prepared via S/NS process. Up to 0.75 g of CL-20 and 0.25 g of β-CD (mass ratio 3:1) were mixed into 25 mL of DMAc at 25 °C. The solution was then slowly poured into 100 mL of distilled water at 0 °C followed by stirring for several hours. The solution was then filtrated. The product was washed five times with 2000 mL of distilled water to remove β-CD. To fully dissolve β-CD, the solution was kept at static conditions at 30 °C for 24 h each time. The sample was finally obtained by freeze-drying. The CL-20 was recrystallized without β-CD via the same method. The samples were then stored in a desiccator until used. Prior to material characterizations, the samples were further dried by heating at 100 °C for 48 h in a vacuum oven.

Computational Details

Based on the crystallographic data of α-CL-20 (CSD: PDF2#: 00-052-2431), the unit cell model without water molecule was constructed.

MD Simulation: All MD simulations were performed by the Discover code of the commercial molecular modeling software package Materials Studio 5.5[1] by using the compass force field.[2] Anderson thermostat was used to control the system.[3] MD simulation was performed in an NVT at the temperature of 298 K.[3] For the equilibration stage, the time step for the MD simulation is 1 fs with a period of 100 ps.[4] The Van der Waals and Coulomb interactions were calculated via the standard Ewald and atom-based methods, respectively. The final structure after MD simulation was used as the balance structure of CL-20/β-CD crystal model.

Table S1. The main crystal grown facets of CL-20 crystal

(hkl)	D_{hkl}/Å	$E_{att(Total)}$/kJ·mol^{-1}	$E_{att(vdW)}$/kJ·mol^{-1}	$E_{att(Electrostatic)}$/kJ·mol^{-1}	Percentage of exposed crystal plane (%)
(002)	12.44	−101.20	−49.24	−51.96	44.3
(020)	6.90	−176.87	−84.28	−92.59	11.5
(102)	6.67	−225.28	−98.60	−126.69	1.3
(021)	6.65	−184.02	−84.06	−99.96	10.8
(111)	6.61	−209.62	−90.12	−119.50	32.2

Table S2. Intermolecular hydrogen bonds (IHB) between CL-20 and β-CD molecules

Number of IHB	A	B	C	D	E		F	G	H
					E1	E2			
Length of IHB (Å)	2.079	1.675	-	-	1.962	1.581	-	2.494	1.676

Materials characterizations

The SEM images were obtained using FEI-Nova NanoSEM600 (America). The structure was characterized via X-ray diffraction (XRD, X'Pert PRO, Netherlands). Thermogravimetry-differential scanning calorimetry was performed using NETZSCH STA 449F3 Instrument (Germany). About 2 mg to 5 mg of the sample was weighed into crimped aluminum pans, pierced to allow vapor to escape, and pressed to increase contact between the pan and the sample. Measurements were recorded with 60 mL·min^{-1} air purge flow at 10 °C min^{-1} from 25 °C to 500 °C for each sample. The purity of the samples was determined via HPLC (Agilent 7890A, America) with C18 column, and the mobile phase consists of acetonitrile–water (volume ratio 60:40). Nitrogen sorption isotherms were measured using Quadrasorb SI (America) at −196 °C. Prior to measurements, the samples were degassed at 100 °C in vacuum for 10 h.

The impact sensitivity test is similar to that in Ref. [5, 6]. A 30 mg sample was placed between

steel anvils and was hit by a 2 kg hammer. The environmental temperature and humidity are at 25 °C and 20%. A total of 25 samples were tested. Initiation was defined as any evidence of flash, flame, or explosion that occurred during impact.

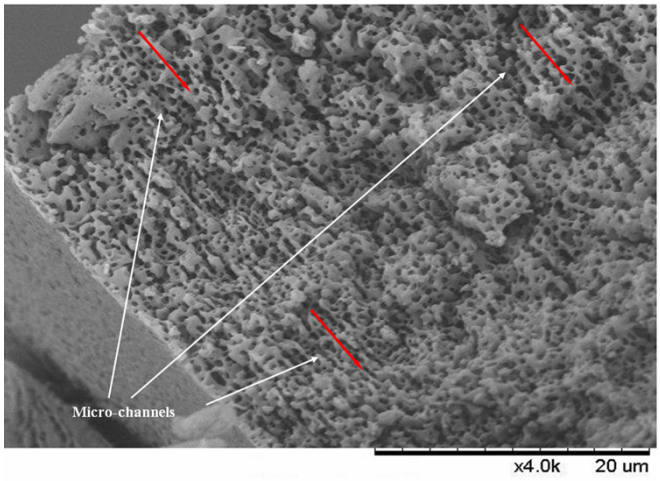

Fig. S1 SEM of porous CL-20

Table S3 Summarized results for DSC experiments of porous CL-20 and ε-CL-20

samples	phase transition temperature (ºC)	decomposition peak temperature (ºC)	reaction enthalpy $J \cdot g^{-1}$
porous CL-20	159.2	232.3	1975.8
ε-CL-20	152.5	235.6	1980.3

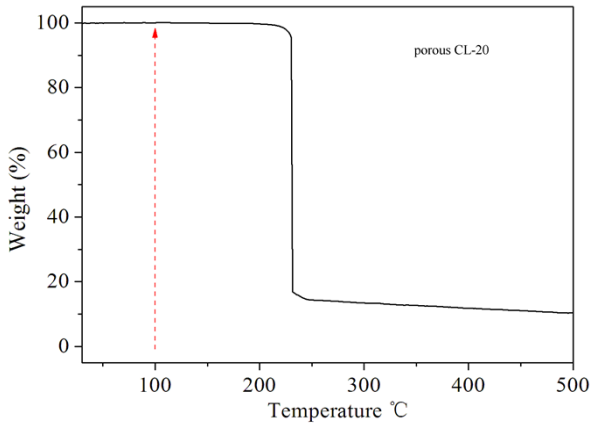

Fig. S2 TG of porous CL-20

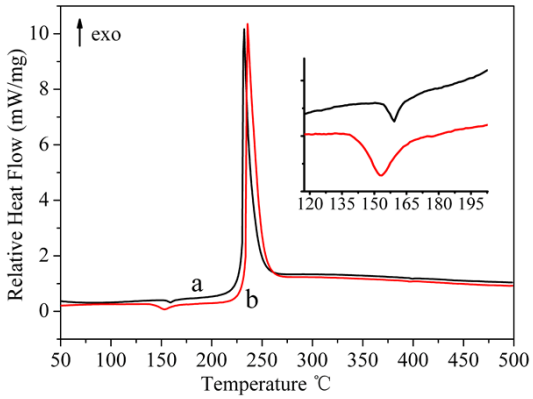

Fig. S3 DSC of (a) porous CL-20 and (b) ε-CL-20

Impact Sensitivity tests

Table S4 Critical height H_{50} of high explosives

Name of high explosives	ε-CL-20	α-CL-20	porous CL-20
H_{50} (cm)	21	19	49

Reference

[1] Materials Studio 5.5 Molecular Modeling System. Accelrys Inc., San Diego, CA, 2010.

[2] Sun, H. J. Chem. Phys. B 1998, 102, 7338-7364.

[3] Andersen, H. C. J. Chem. Phys. 1980, 72, 2384-2395.

[4] Jin P. Shen, Xiao H. Duan, Qing P. Luo, Yong Zhou, Qiaoliang Bao, Yong J. Ma, Chong H. Pei, Cryst. Growth Des. 2011, 11, 1759-1765.

[5] W. J. Dixon, A. M. Mood, J. Am. Stat. Assoc. 1948, 43, 109-126.

[6] R. Li, J. Wang, J.P. Shen, C. Hua, G.C. Yang, Propell. Explos. Pyrot., 2013, 38, 798-804.