Supplementary Materials for

Largely Desensitized and Stabilized CL-20 Crystals through reinforcement Cross-linked Graphene Oxide

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S1. Experimental

In the preparation process, the amount of GO-TAG is strict to 1.5 wt%, and due to the latter large amount of TAGN added, the amount of GO-TAG can be regarded as GO. A series of samples with different TAGN content (the molar ratio of CL-20 to TAGN changes from 3:1 to 8:1) has been fabricated, and they were named according to the different content, but in this article, in order to describe easier, the corresponding labels were used instead of the name. The details about the experiment have been demonstrated in Table S1. In this work, the product batch charge is calculated by the molar ratio, and the other obtained data such as density, particle size distribution, friction/impact sensitivity were experimentally measured. The detonation parameters and specific impulse were obtained by using EXPLO-5 software.

Table S1. Table of preparation ratio and naming rules.

Name	Corresponding label	Molar ratio	m_{GO-TAG}(mg)	m_{TAGN}(mg)	m_{CL-20}(mg)	$V_{glyoxal}$(μl)
CL-20/GO-TAGP-3/1	CL-20-1	3:1	23.3	250	1972.5	68.0
CL-20/GO-TAGP-4/1	CL-20-2	4:1	24.0	200	2106.0	54.7
CL-20/GO-TAGP-5/1	CL-20-3	5:1	22.0	150	1974.0	41.03
CL-20/GO-TAGP-6/1	CL-20-4	6:1	17.3	100	1579.0	27.4
CL-20/GO-TAGP-7/1	CL-20-5	7:1	20.0	100	1842.0	27.4
CL-20/GO-TAGP-8/1	CL-20-6	8:1	22.6	100	2105.0	27.4

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Notes: Molar ratio means CL-20 to TAGN.

Preparation of GO-TAG precursor: 400 mg GO was dispersed in 200 ml H_2O by high power ultra-sonication in a glass reactor. Add 10 ml aqueous mixed solution of EDC (80 mg) and NHS (60 mg) to the dispersed GO, stirring for 60 min. The black agglomeration was formed. Then 4 g of TAGN was added to the obtained mixture in the glass reactor, which should be kept in a water bath with controlled temperature of 60~65 °C for two hours using a magnetic stirring. The black flocculent precipitates were gradually formed, which was filtrated and washed by distilled water for three times. The filtrated liquid has a PH value of 1.5-2.0 due to presence of HNO_3 molecule.

Preparation of mechanical mixing CL-20/GO-TAGP-M: This procedure can be described as follow: Certain amount of TAGN was added to the dispersion of GO-TAG (in DMSO), reacted at 100°C for 1 hour to generate energetic cross-linked GO. After forming the cross-linked GO-TAGP, the dispersion was washed twice with ethyl acetate by centrifugation method. For making the uniform EAC dispersion of GO-TAGP, sonication method was used (10 min). Then the ε-CL-20 crystals were added to the abovementioned dispersion and stirred at room temperature. After completely dissolving of CL-20, trichloromethane was added to co-precipitate GO-TAGP with nano-sized CL-20 to obtain mechanical mixing CL-20/GO-TAGP-M. Then the product was washed by trichloromethane, filtered and lyophilized.

S2. Characterization

The scanning electron microscopy (SEM) analysis was operated on a Quanta FEG 250, with an accelerating voltage 15 or 20 kV. Meanwhile, the products had to be coated by gold to get better electron conductivity. More detailed compositions and structure information can be obtained by Transmission electron microscopy (TEM). The TEM analysis was operated on a Tecnai G2 F20, by which the target samples were dispersed in ethanol, so that they can achieve a maximum magnification of 1 million times at an accelerating voltage of 200 kV. The compositions of the samples and the crystal phases of the elements were characterized by powder X-ray diffraction (XRD, Panaco Sharp Xpert Pro MPD; Bruker C2 Discover with GADDS, operating at 40 kV and 40mA with unfiltered Cu Kα radiation, E1/48049 eV, k1/41.5406 Å). Differential scanning calorimeter (DSC) curves were conducted with a TA

Instruments DSC Q200. X-ray photoelectron spectroscopy (XPS) was acquired from Thermo VG 250 (USA). The standard BAM (BFH-10, Czech) device was used to evaluate the impact and friction sensitivity of sample displaying the form of impact energy and friction force. We selected the minimum explosion position and the maximum non-explosion height for the BAM friction and impact sensitivity, respectively. Each round evaluation needs 40 mg explosive, and every explosive need to be tested consecutively for 6 times. The transformation of calorific value was investigated by a standard oxygen bomb calorimeter. Element analysis (EA) was conducted with Elementar vario EL clube, with an instrument error less than 0.1%.

S3 Supporting Figureures and Tables

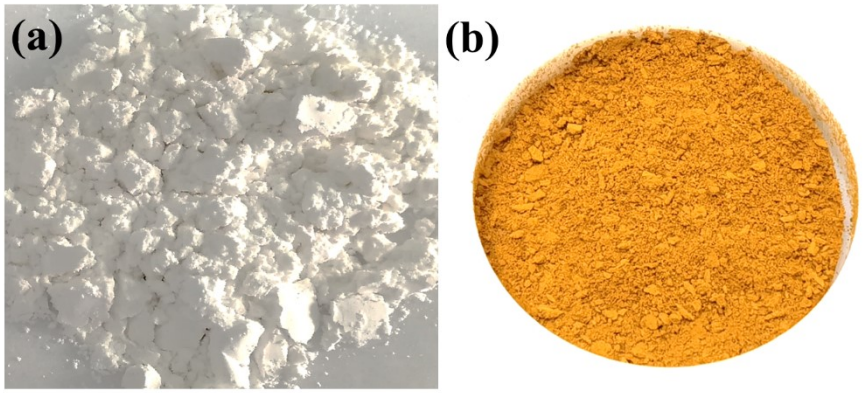

Figure S1. The digital photos of (a) ε-CL-20; (b) TAGP.

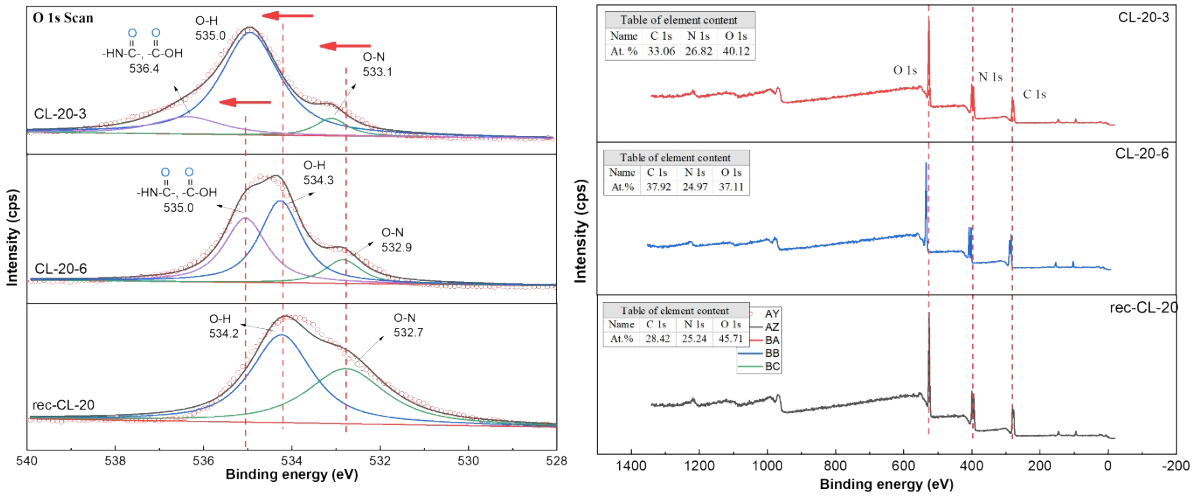

Figure S2. High-resolution XPS spectra of O 1s and survey peaks for rec-CL-20, CL-20-3 and CL-20-6

Table S2. Detailed binding energy parameters for rec-CL-20 and assembled CL-20 crystals (C 1s

and N1s)

Elements		C 1s				N 1s		
bonding		C-C	C-H	C=C	C-N	-COOH, -NHC=O	N-N	N-H	N-O
rec-CL-20	Location	285.0		-	288.8	-	401.7	-	407.4
	FWHM	3.19		-	1.77	-	2.61	-	2.28
	Area	20008.7		-	13252.7	-	26645.5	-	15306.7
	Percentage	60.2%		-	39.8%	-	63.5%	-	36.5%

bonding		C-C	C=C	C-H	C-O-C	-COOH -NHC=O	N-N	N-H	N-O
CL-20-6	Location	285.0	286.0	286.8	289.4	402.5	403.3	408.4	
	FWHM	0.57	0.61	0.93	1.29	1	1.39	1.49	
	Area	6712.9	8779.2	5564.5	17929.3	6508.9	17706.1	18056.6	
	Percentage	17.2%	22.5%	14.3%	46.0%	15.4%	41.9%	42.7%	
CL-20-3	Location	285.0	286.0	286.8	289.5	402.9	403.6	408.8	
	FWHM	0.63	0.7	1.18	1.55	1.22	1.17	1.26	
	Area	5003.6	7007.3	6617.4	22451.6	14890.6	11721.2	22490.0	
	Percentage	12.2%	17.1%	16.1%	54.6%	30.3%	23.9%t	45.8%	

Table S3. Detailed binding energy parameters of rec-CL-20 and assembled CL-20/GO-TAGP crystals (O1s)

Element		O 1s		
bonding		O-N	O-H	O=C
rec-CL-20	Location	532.7	-	534.2
	FWHM	2.1	-	1.65
	Area	28979.3		36372.6
	Percentage	44.3%	-	55.7%
CL-20-6	Location	532.9	534.3	535.0
	FWHM	0.91	1.22	1.08
	Area	8140.1	42044.3	22533.93
	Percentage	11.2%	57.8%	31.0%
CL-20-3	Location	533.1	535.0	536.4

	FWHM	0.86	1.58	1.81
	Area	5926.5	63712.8	12311.4
	Percentage	7.2%	77.7%	15.0%

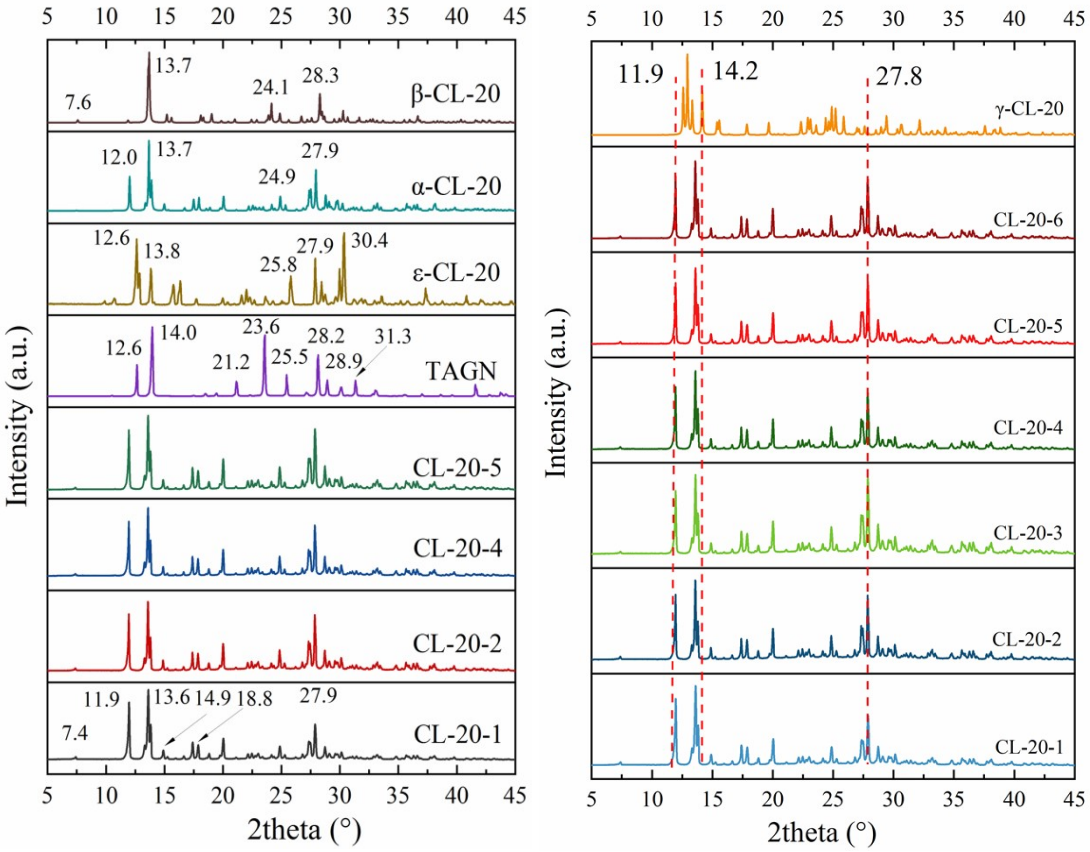

Figure S3. The X-ray powder diffraction spectra of standard α-, β-, ε-, γ-CL-20 and assembled CL-20 hybrid crystals

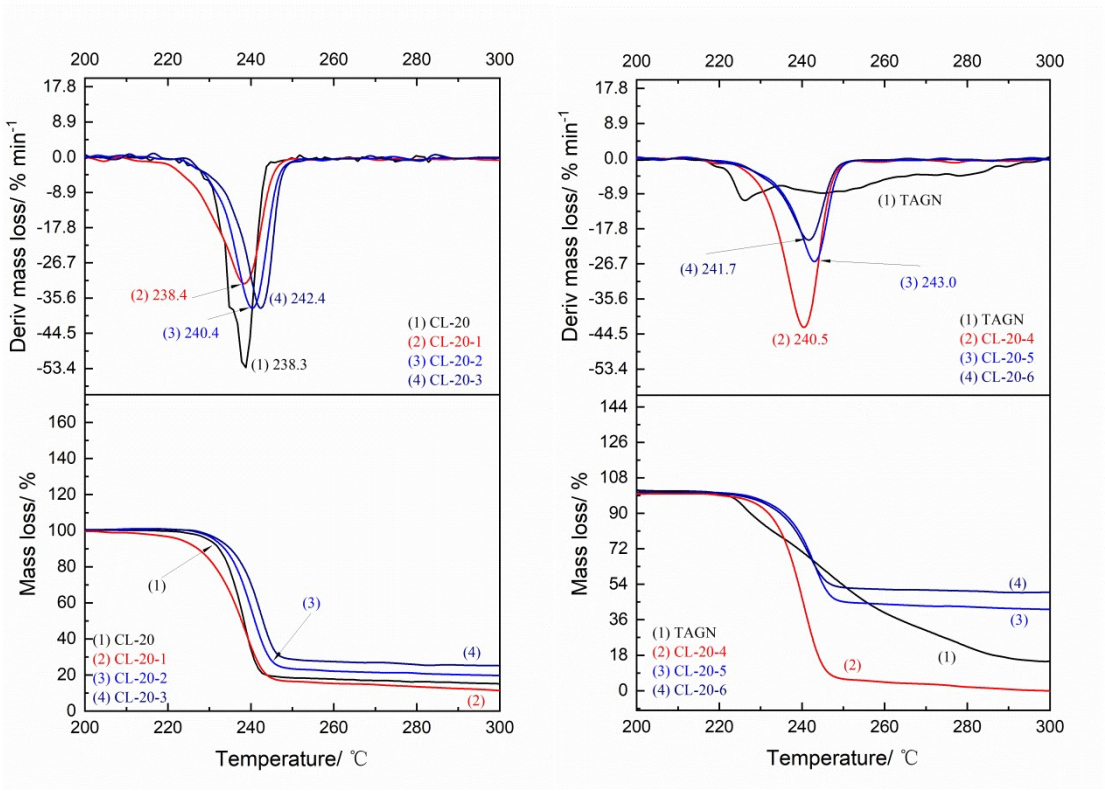

Figure S4. The TG-DTG curves of modified CL-20 and pristine rec-CL-20 at heating rate of 5 °C·min^{-1}

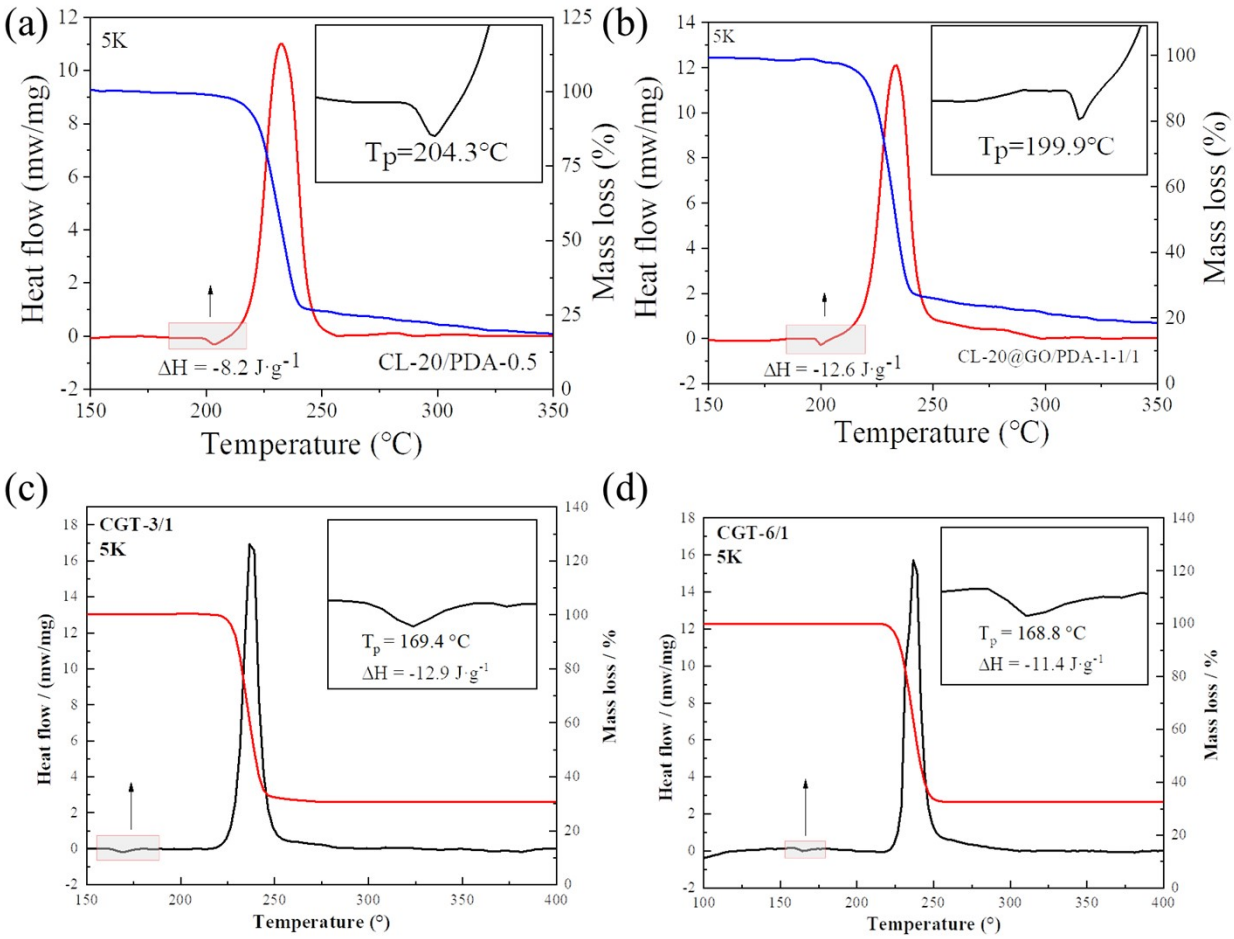

Figure S5. The TG-DSC curves of modified CL-20 at heating rate of 5 °C·min^{-1}