

## Supplementary Materials

# Sustainable Multi-Network Cationic Cryogels for High-Efficiency Removal of Hazardous Oxyanions from Aqueous Solutions

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**Figure S1.** FTIR spectra of SN5, DN5 and TN5.2 composites (sample codes are the same with those in Table 1).

**Figure S2.** FTIR spectra of DN20.3 and TN20.3 composite sponges (sample codes are the same with those in Table 1).

**Table S1.** Values of the average pore diameters and pore wall thicknesses of composite cryogels.

**Table S2.** Elemental analysis given by EDX spectra of SN5, SN20 and some DN and TN composite cryogels (sample codes are from Table 1).

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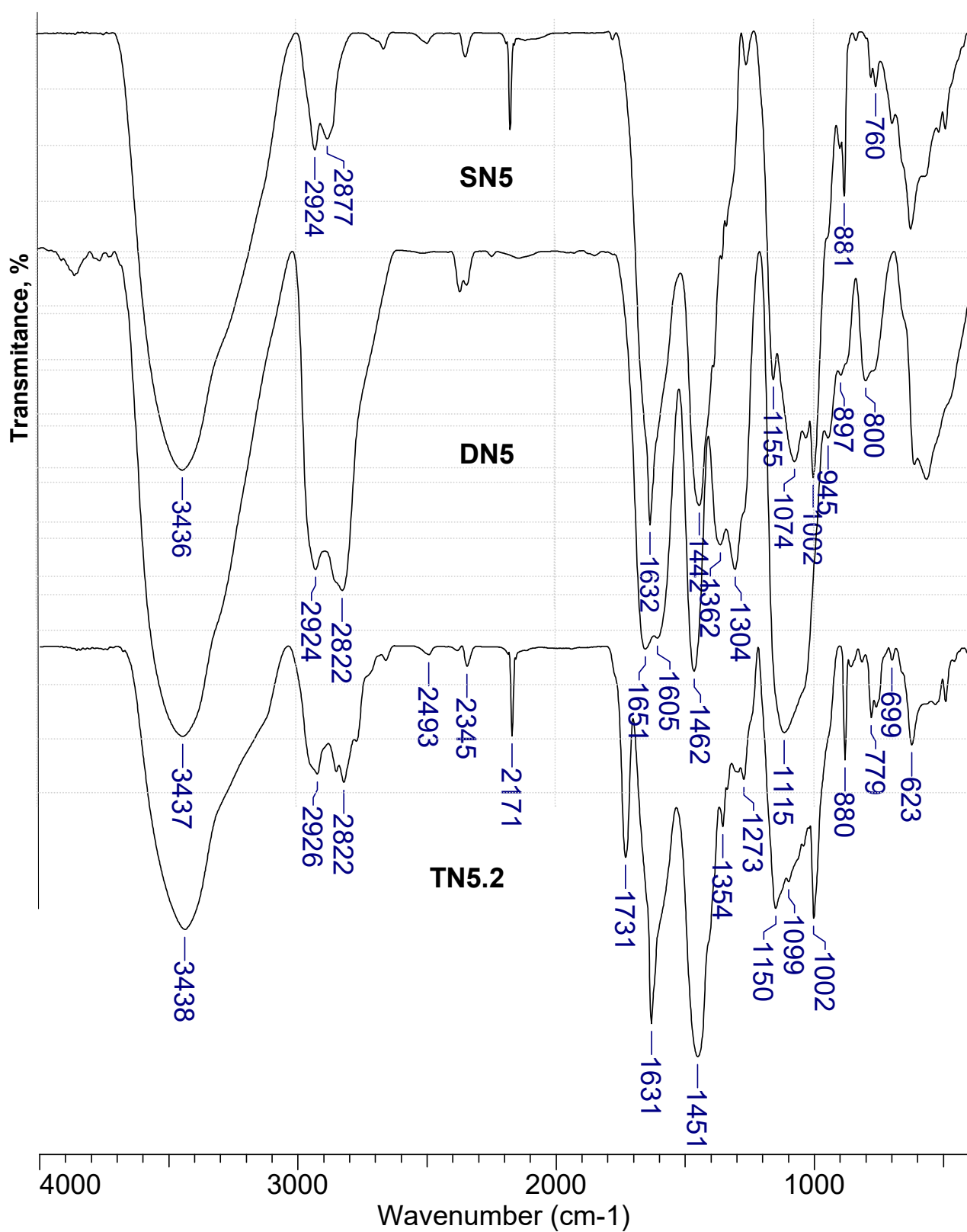
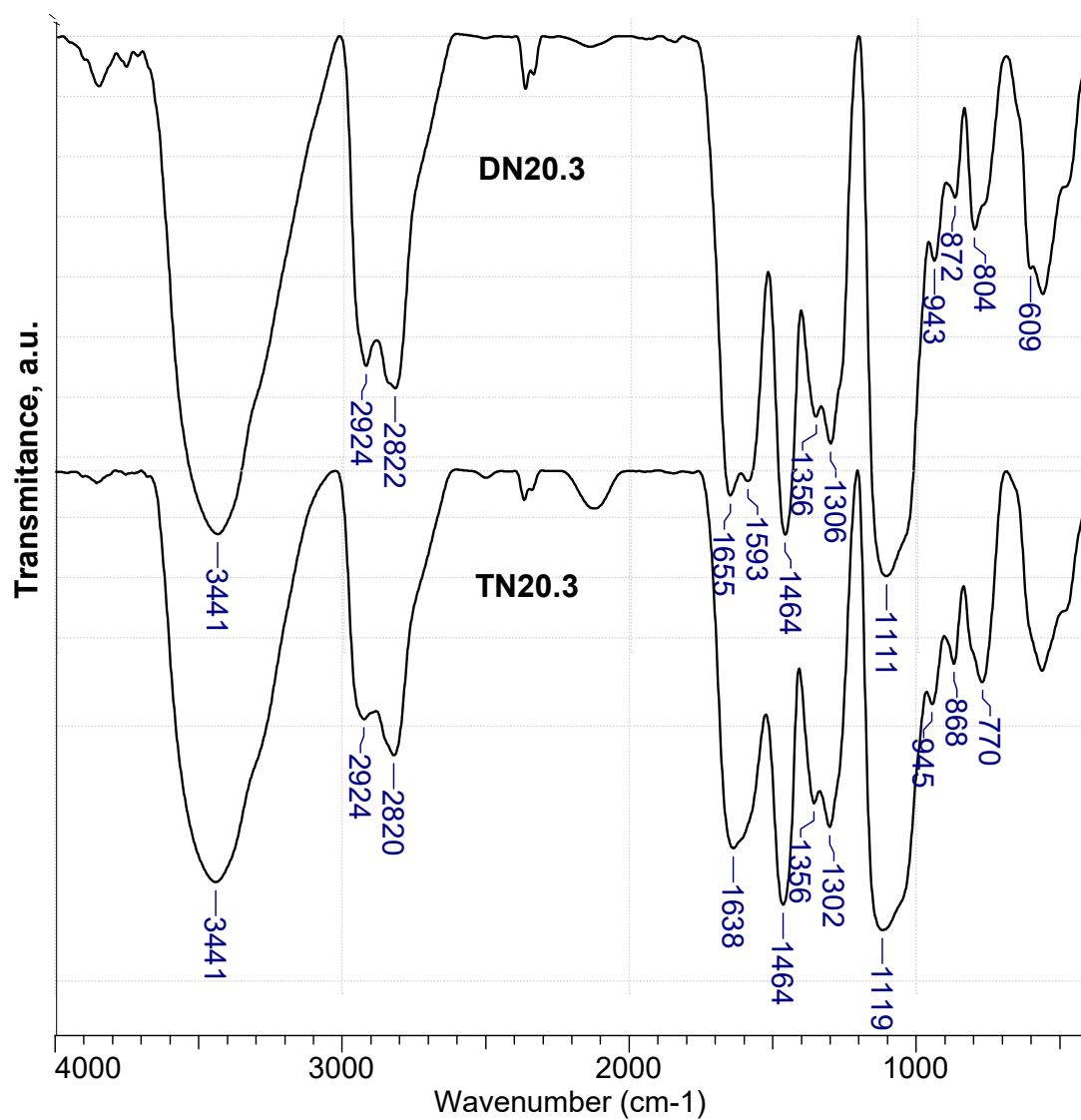


Figure S1. FTIR spectra of SN5, DN5 and TN5.2 composites (sample codes are from Table 1).



**Figure S2.** FTIR spectra of DN20.3 and TN20.3 composite sponges (sample codes are from Table 1).

**Table S1.** Values of the average pore diameters and pore wall thicknesses of composite cryogels.

Sample	Average pore diameter, $\mu\text{m}$	Pore wall thickness, $\mu\text{m}$
SN5	$141.81 \pm 32.56$	$3.50 \pm 0.83$
DN5	$56.73 \pm 12.28$	$10.02 \pm 2.25$
TN5.1	$25.53 \pm 4.27$	$18.64 \pm 5.21$
TN5.2	$53.18 \pm 6.72$	$20.94 \pm 2.14$
SN20	$107.83 \pm 15.47$	$5.73 \pm 1.46$
DN20.2	$51.41 \pm 8.71$	$12.95 \pm 4.87$
TN20.2	$35.28 \pm 5.44$	$20.76 \pm 3.08$

TN20.3	28.08 ± 7.09	24.77 ± 4.37
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**Table S2.** Elemental analysis given by EDX spectra of SN5, SN20 and some DN and TN composite cryogels (sample codes are from Table 1).

Sample Code	C, wt.%	N, wt.%	O, wt.%
SN5	52.5 ± 0.15	9.5 ± 0.25	37.2 ± 0.4
DN5	63.25	12.96	23.79
TN5.1	47.46 ± 0.61	25.67 ± 2.12	26.87 ± 1.97
TN5.2	67.31	13.35	17.33
SN20	57.72 ± 3.06	7.77 ± 0.84	34.51 ± 2.29
DN20.2	67.84 ± 0.05	19.14 ± 0.51	12.96 ± 0.46
TN20.2	65.99 ± 0.5	20.45 ± 0.06	12.54 ± 0.55

**Table S3.** Swelling ratio (SR) and equilibrium water content (EWC) of the SN, DN and TN cryogels.

Sample Code	SR	EWC, %
SN5	64.69	98.45
DN5	9.605	89.59
TN5.1	9.48	89.33
TN5.2	9.142	89.06
SN20	45.25	97.79
DN20.1	8.52	88.95
TN20.1	6.745	85.17
DN20.2	9.17	89.87
TN20.2	8.24	87.98
DN20.3	9.011	88.903
TN20.3	8.151	87.73

**Table S4.** Values of the compressive elastic modulus for single network cryogels as a function of number of compression cycles.

Sample code	Number of compression cycle	Compressive elastic modulus, kPa	R <sup>2</sup>
SN5	1	7.74	0.999
	2	4.52	0.998
	3	4.14	0.998
	4	4.17	0.998
	5	3.48	0.998
SN20	1	3.54	0.998
	2	3.52	0.997
	3	3.22	0.999
	4	2.66	0.984
	5	2.04	0.999

**Table S5.** Kinetic parameters for the adsorption of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions onto multi-network composite cryogels constructed onto SN5 cryogel as the first network.

Kinetic model	Parameters	SN5	DN5	TN5.1	TN5.2
PFO	$q_e^{exp}$ , mg/g	102.19	121.38	133.28	133.33
	$q_e^{calc}$ , mg/g	99.63	118.56	129.4	130.99
	$k_1$ , min <sup>-1</sup>	0.0331	0.0283	0.0436	0.05767
	R <sup>2</sup>	0.9614	0.9553	0.9591	0.9791
	$\chi^2$	35	58	59	30
PSO	$q_e^{calc}$ , mg/g	105.83	126.3	136.6	136.6
	$k_2$ , g mg <sup>-1</sup> min <sup>-1</sup>	5.213 x 10 <sup>-4</sup>	3.732 x 10 <sup>-4</sup>	5.396 x 10 <sup>-4</sup>	7.864 x 10 <sup>-4</sup>
	R <sup>2</sup>	0.9909	0.9866	0.9927	0.9954
	$\chi^2$	8	17	11	6.5
Elovich	$\alpha$ , mg g <sup>-1</sup> min <sup>-1</sup>	150.5	85.75	808	15076
	$\beta$ , g mg <sup>-1</sup>	0.086	0.0668	0.0777	0.1009
	R <sup>2</sup>	0.945	0.9427	0.9562	0.9552
	$\chi^2$	50	75	64	63

**Table S6.** Kinetic parameters for the adsorption of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> anions onto SN20 and DN composite cryogels having SN20 as the first network.

Kinetic model	Parameters	SN20	DN20.1	DN20.2	DN20.3
	$q_e^{exp}$ , mg/g	93.41	109.34	127.59	123.76
	$q_e^{calc}$ , mg/g	91.37	106.68	124.2	120.98
	$k_1$ , min <sup>-1</sup>	0.0271	0.033	0.032	0.0295

PFO	$R^2$	0.9598	0.9566	0.953	0.9566
	$\chi^2$	32	45	66	59
PSO	$q_e \text{ calc, mg/g}$	97.47	113.2	132	128.72
	$k_2, \text{g mg}^{-1} \text{ min}^{-1}$	$4.594 \times 10^{-4}$	$4.904 \times 10^{-4}$	$4.047 \times 10^{-4}$	$3.835 \times 10^{-4}$
	$R^2$	0.9877	0.9881	0.9878	0.9864
	$\chi^2$	9.6	12	17	18
	$\alpha, \text{mg g}^{-1} \text{ min}^{-1}$	61.15	168	163.1	2542
Elovich	$\beta, \text{g mg}^{-1}$	0.0845	0.0808	0.0678	0.0972
	$R^2$	0.9411	0.9444	0.9474	0.9111
	$\chi^2$	46	57	74	23

**Table S7.** Kinetic parameters for the adsorption of  $\text{Cr}_2\text{O}_7^{2-}$  anions onto TN composite cryogels constructed onto SN20 cryogels.

Kinetic model	Parameters	TN20.1	TN20.2	TN20.3
	$q_e \text{ exp, mg/g}$	131.75	132.8	133.3
PFO	$q_e \text{ calc, mg/g}$	128.3	128.8	130.3
	$k_1, \text{min}^{-1}$	0.02576	0.0382	0.0479
	$R^2$	0.9576	0.9579	0.9708
	$\chi^2$	66	64	42
	$q_e \text{ calc, mg/g}$	137.2	137.2	136.91
PSO	$k_2, \text{g mg}^{-1} \text{ min}^{-1}$	$3.0605 \times 10^{-4}$	$3.791 \times 10^{-4}$	$6.104 \times 10^{-4}$
	$R^2$	0.9891	0.9917	0.9947
	$\chi^2$	17	13	8
	$\alpha, \text{mg g}^{-1} \text{ min}^{-1}$	67.64	147.67	194.3
Elovich	$\beta, \text{g mg}^{-1}$	0.0581	0.0641	0.0845
	$R^2$	0.9477	0.9513	0.9519
	$\chi^2$	82	74	69

**Table S8.** Kinetic parameters for the adsorption of  $\text{H}_2\text{PO}_4^-$  anions onto multi-network composite cryogels.

Kinetic model	Parameters	DN20.1	DN20.2	TN20.1	TN20.2	TN5.1
	$q_e \text{ exp, mg/g}$	103.27	127.01	128.64	123.63	128.55
	$q_e \text{ calc, mg/g}$	100.49	123.88	126.76	121.86	125.97
	$k_1, \text{min}^{-1}$	0.0318	0.0361	0.0212	0.0221	0.0292

PFO	$R^2$	0.9506	0.9661	0.9757	0.9683	0.9663
	$\chi^2$	46	47	39	46	50
PSO	$q_e$ calc, mg/g	106.8	131.32	136.4	131.04	134.1
	$k_2$ , g mg <sup>-1</sup> min <sup>-1</sup>	4.981 x 10 <sup>-4</sup>	4.596 x 10 <sup>-4</sup>	2.454 x 10 <sup>-4</sup>	2.6803 x 10 <sup>-4</sup>	3.618 x 10 <sup>-4</sup>
	$R^2$	0.9865	0.9932	0.9882	0.9914	0.9885
	$\chi^2$	12	9	19	12	17
Elovich	$\alpha$ , mg g <sup>-1</sup> min <sup>-1</sup>	129.45	282	33.3	36.42	114.7
	$\beta$ , g mg <sup>-1</sup>	0.0836	0.0727	0.0531	0.0563	0.0639
	$R^2$	0.9471	0.9454	0.9314	0.9437	0.9357
	$\chi^2$	49	75	110	83	95

**Table S9.** Selectivity coefficients for the sorption of oxyanions in binary systems.

Sample Code (see Table 1)	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>			H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>			$k_{H_2PO_4^-}^{Cr_2O_7^{2-}}$
	C <sub>e</sub> , mg/L	q <sub>e</sub> , mg/g	$K_{dCr_2O_7^{2-}}$	C <sub>e</sub> , mg/L	q <sub>e</sub> , mg/g	$K_{dH_2PO_4^-}$	
SN5	26.85	97.53	3.63	30.54	92.61	3.03	1.19
TN5.2	2.14	130.48	60.97	5.72	125.71	21.98	2.77
SN20	32.18	90.42	2.81	35.09	86.54	2.47	1.14
DN20.1	21.54	1044.61	4.86	28.47	95.38	3.35	1.45
DN20.2	8.69	121.74	14.01	10.41	119.46	11.48	1.28
TN20.3	2.97	129.37	43.56	7.14	123.82	17.34	2.51

$$k_{H_2PO_4^-}^{Cr_2O_7^{2-}} = \frac{K_{dCr_2O_7^{2-}}}{K_{dH_2PO_4^-}}$$

**Table S10.** Comparative results for the sorption of Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> anions by multi-network cryogels and by different sorbents from literature.

Sorbent				Ion	pH	Temp., °	Sorbent	q <sub>m</sub> , mg/g	Ref.*
						C	dose, g/L		
Weak base anion exchange resin				Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	4	25	0.6	194	[10]
impregnated with EPIDMA									
3D-Ordered Macroporous Cross-Linked PS-g-PDMAEMA				Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	4	25	0.4	400	[12]
Amidoxime sorbent				Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	5	25	~ 0.444	130.65	[13]
Strong base anion exchanger embedded into CS/PVAm cryobeads				Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	5.5	25	1.25	318	[14]
Magnetite modified chitosan				Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	3	25	3	58.14	[16]

cinnamaldehyde							
TN5.2(CS/PEI18/PDMAEMA)	Cr <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	4	25	0.75	439	This work	
Zirconium molybdate and macroporous anion exchange resin (ZMAE)	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	5.5	25	0.5	26.1**	[19]	
Quaternary ammonium salt of cotton linter	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	7	30	~ 6.7	30.13	[21]	
Zr-loaded magnetic CS/PVA IPN hydrogel	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	6.5	22 ± 1	0.25	50.76**	[22]	
Zr(IV)-crosslinked carboxymethyl cellulose/carboxymethyl chitosan hydrogels	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	2	25	n.p.	93.5	[23]	
TN20.2(CS/PEI25/PEI18)	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	4	23	0.75	391.1	This work	
TN5.2(CS/ PEI18/PDMAEMA)	H <sub>2</sub> PO <sub>4</sub> <sup>-</sup>	4	23	0.75	422.45	This work	

\*The number of references is identical with that given in the main text. \*\*mg-P/g sorbent.