Supporting Information

Flexible and Binder-Free Hierarchical Porous Carbon Film for Supercapacitor Electrodes Derived from MOFs/CNT

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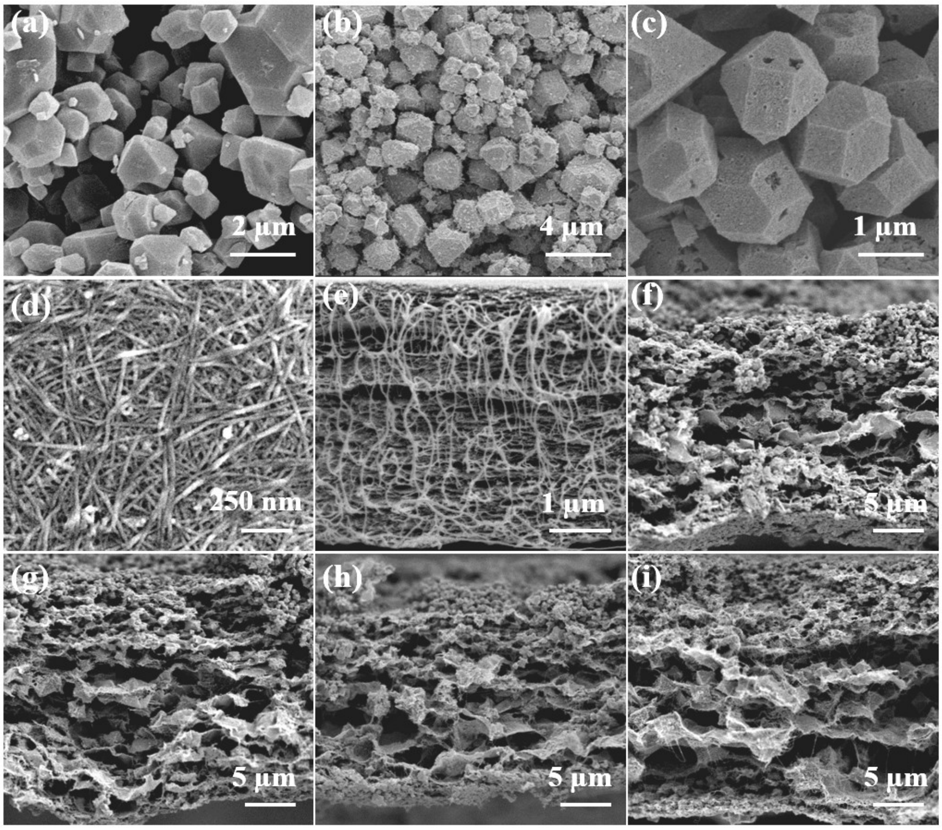

Fig S1. SEM images of HKUST-1 crystals (a) before calcination, (b) after calcination, (c) after acid treatment; (d), (e) and (f) is the surface and cross section of CHNs/CNT; (f), (g), (h) and (i) the cross section of HPCF1, 2, 3 and 5, respectively.

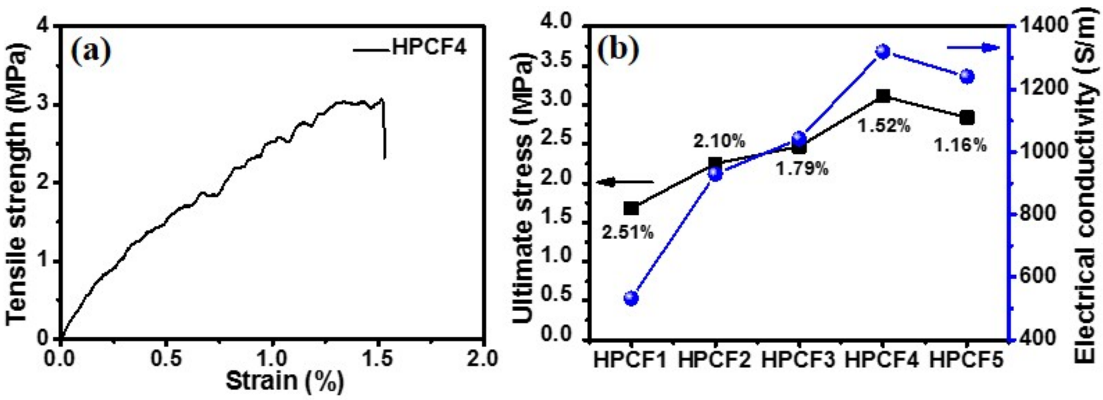

Fig S2. (a) Tensile strength–strain curves of HPCF4; (b) Ultimate stress, strain and electrical conductivity for HPCF1, 2, 3, 4 and 5.

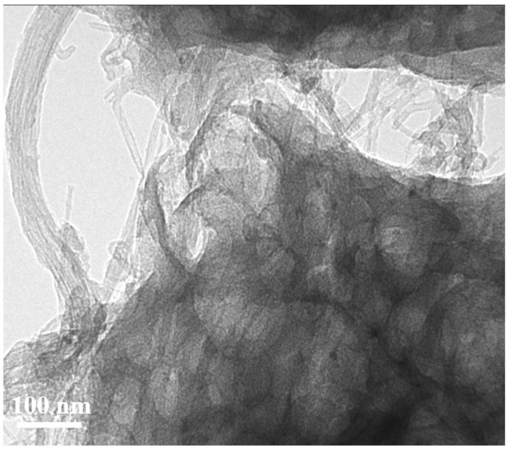

Fig S3. High magnification TEM of HPCF4.

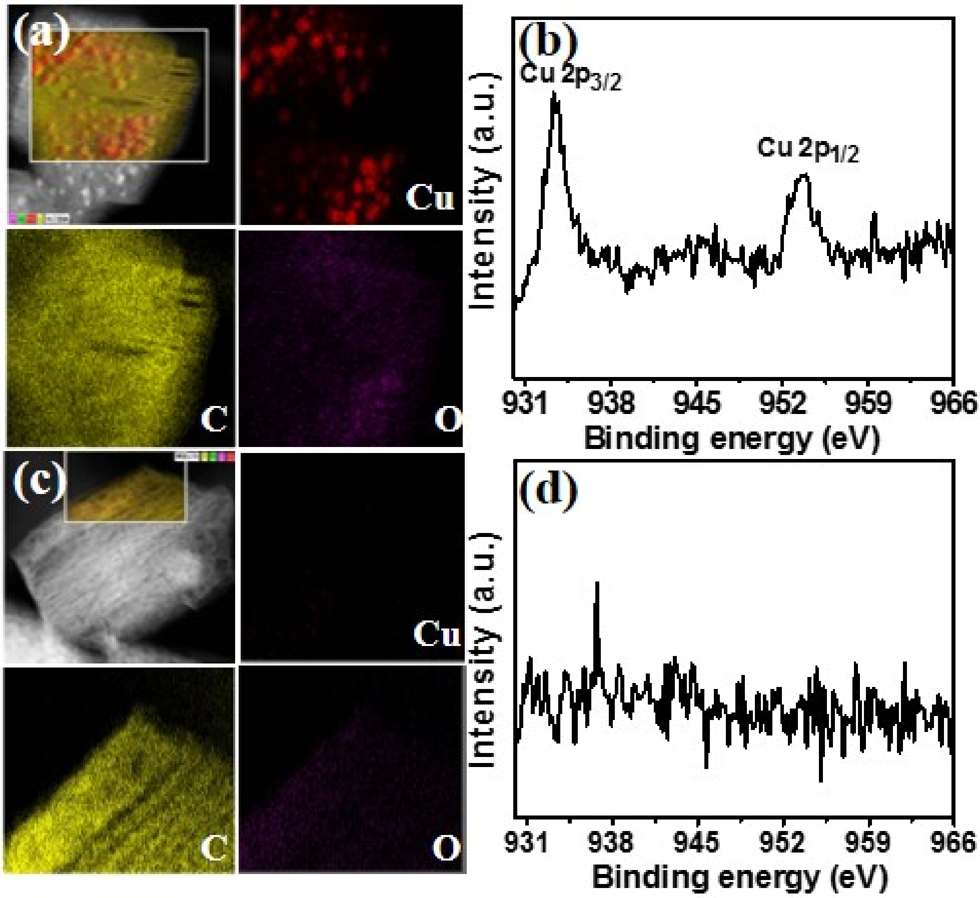

Fig S4. TEM images of PCF4. (a) before and (c) after acid treatment; (b) and (d) is the Cu 2p XPS spectra of (a) and (c).

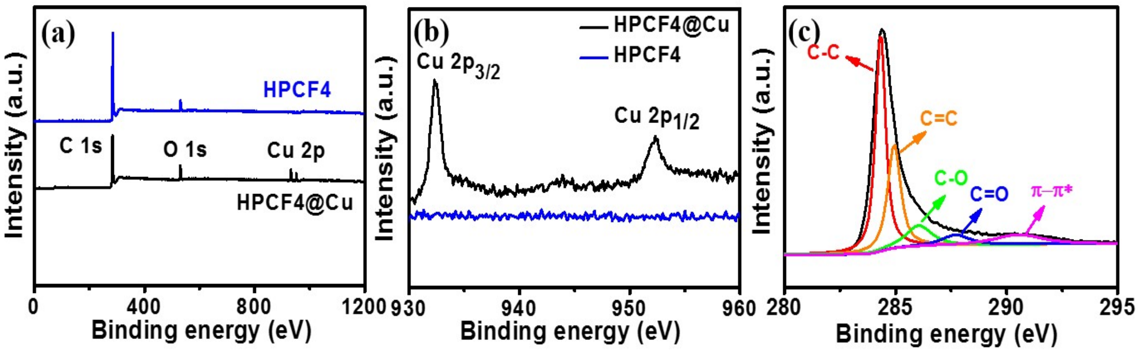

Fig S5. (a) and (b) Overview XPS spectra and Cu 2p spectra of HPCF4 and HPCF4@Cu; (c) C 1s spectra of HPCF4.

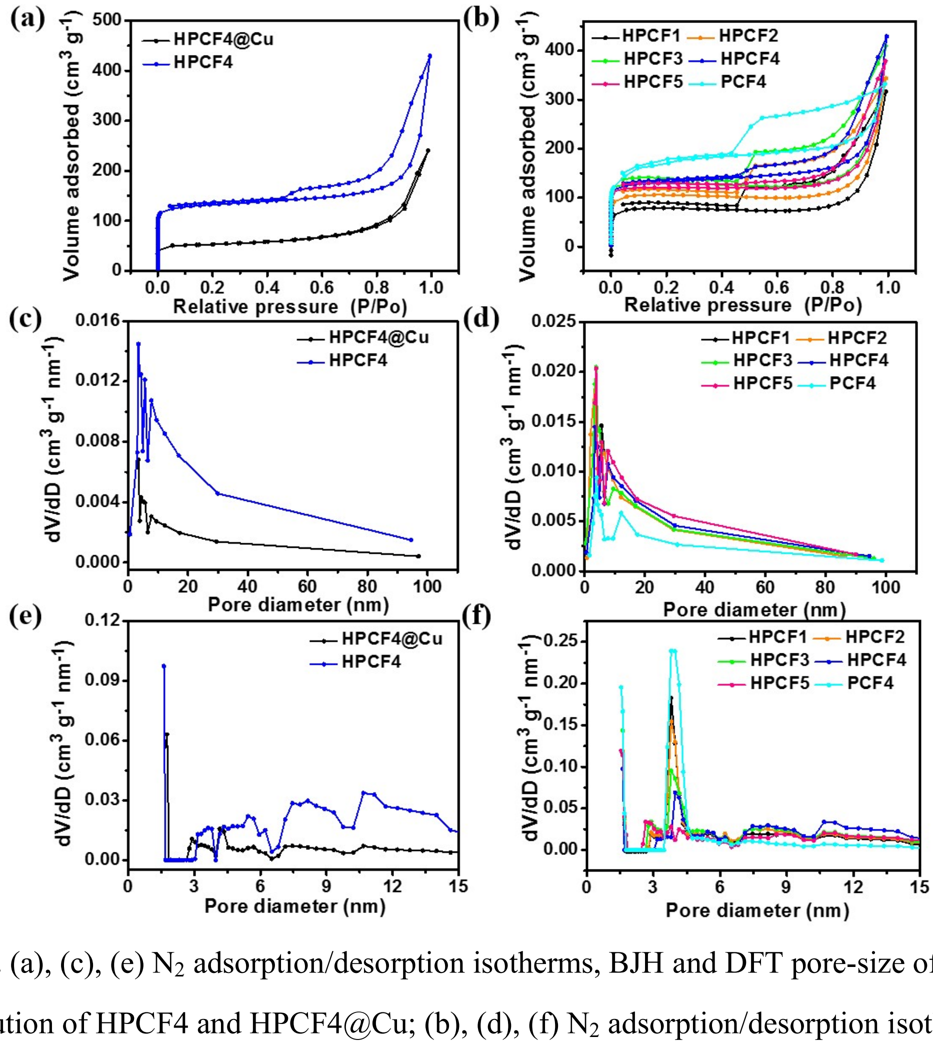

Fig S6. (a), (c), (e) N_2 adsorption/desorption isotherms, BJH and DFT pore-size of distribution of HPCF4 and HPCF4@Cu; (b), (d), (f) N_2 adsorption/desorption isotherms, BJH and DFT pore-size of distribution of the HPCFs.

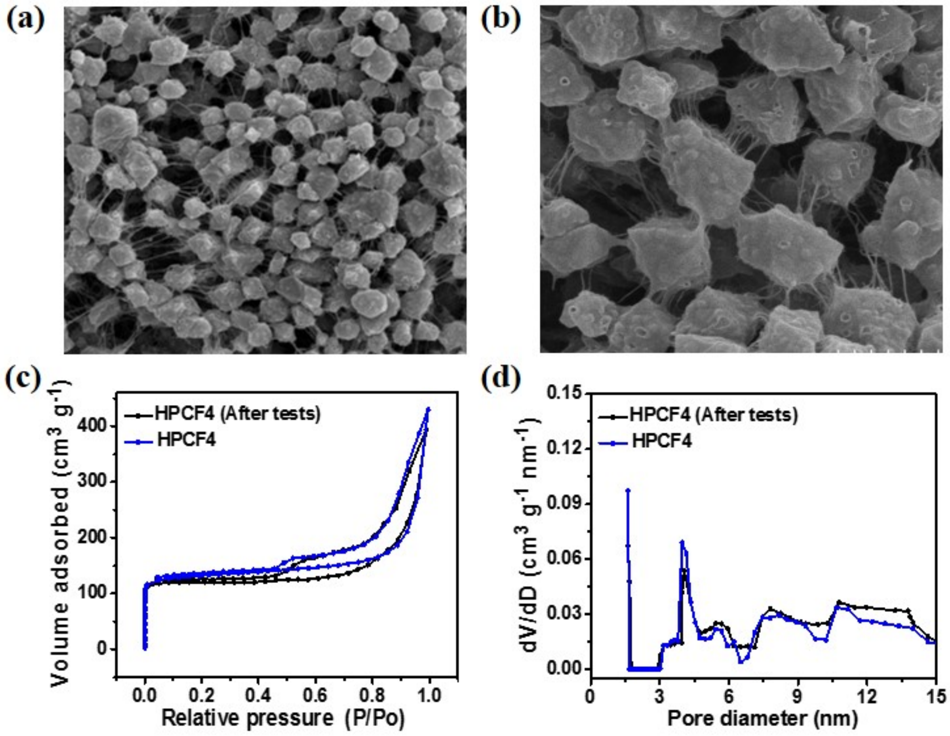

Fig S7. (a) and (b) SEM images, (c) N_2 adsorption/desorption isotherms and (d) DFT pore-size distribution of the HPCF4 sample after long-term cycling tests.

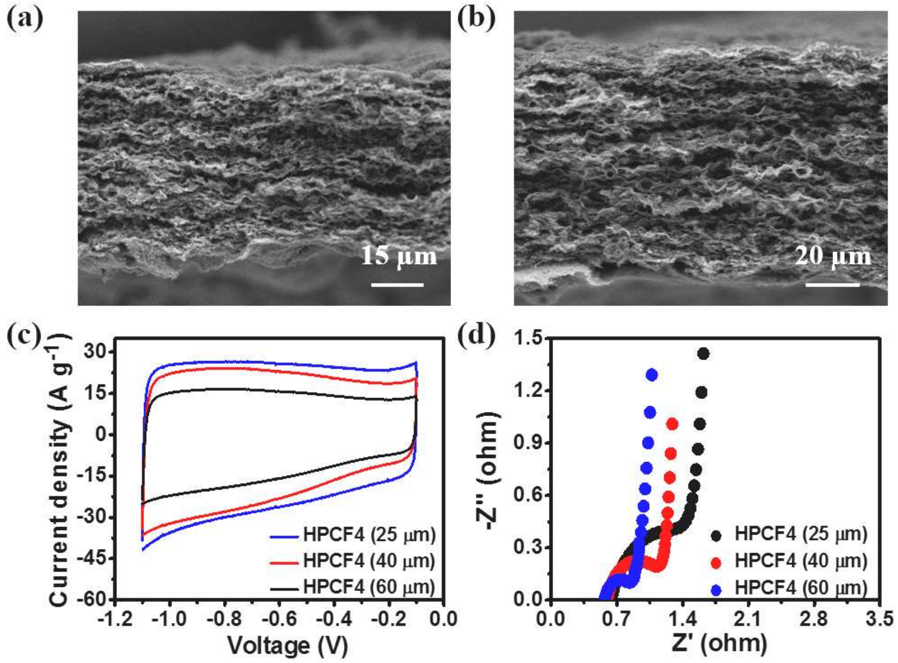

Fig S8. (a) and (b) SEM images of HPCF4 with different thickness; (c) and (d) CV curves and EIS spectra of HPCF4 samples with different thickness.

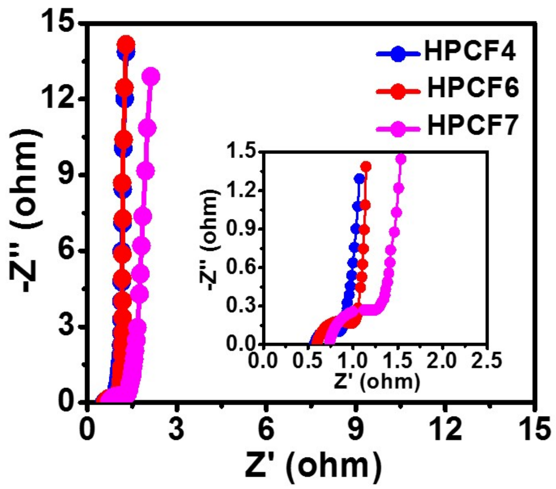

Fig S9. EIS spectra of the HPCF4, 6 and7.

Table S1. Physical and electrochemical properties of the samples.

Sample	XPS [a]/at%			S_{BET} [b]/m^2 g^{-1}	V_t [c]/cm^3 g^{-1}	D_{ave} [d]/nm	σ [e]/S m^{-1}
	C	O	Cu				
HPCF1	93.46	6.47	0.07	330.2	0.44	3.00	532
HPCF2	94.54	5.42	0.04	449.3	0.53	3.39	929
HPCF3	96.11	3.83	0.06	524.9	0.56	3.75	1042
HPCF4	97.43	2.52	0.05	620.1	0.63	3.94	1320
HPCF5	97.86	2.10	0.04	569.3	0.61	3.73	1240
HPCF4@Cu	88.01	6.81	5.18	190.2	0.19	4.00	1310
PCF4				681.3	0.51	5.34	-

[a] Atomic percentage of elements obtained from XPS analysis.[b] Specific surface area calculated by Brunauer-Emmett-Teller (BET) equation.[c] The total pore volume determined from the amount of nitrogen adsorbed at a relative pressure of 0.99.[d] The average pore size was obtained from equation: $D_{ave}= 4*V_t/S_{BET}$ [e] Conductivity was test by four-probe conductivity test.

Table S2. Comparison of the rate performance of flexible or self-standing carbon electrode.

Materials	Electrolyte	Current density/ A g^{-1}	Rate capability retention	Ref
N-doped carbon nanofiber films	6 M KOH	2.5 to 10	0.73	1
N-doped carbon nanofiber network	1 M H_2SO_4	2 to 50	0.57	2
N-doped carbon foam	6 M KOH	1 to 10	0.76	3
GO paper	6 M KOH	2 to 10	0.63	4
graphene oxide/carbon nanotubes	1 M HCl	1 to 100 mV s^{-1}	0.56	5
Porous carbon fibers	3M KOH	2 to 20	0.70	6
Ordered mesoporous carbon	6 M KOH	1 to 10	0.47	7
Activated carbon/CNT	6 M KOH	10 to 100 mV s^{-1}	0.59	8
N-doped carbon microfiers	6 M KOH	1 to 100 mV s^{-1}	0.45	9
Porous carbon fibers	6 M KOH	1 to 100	0.65	10
Hollow carbon nanofiber mats	6 M KOH	1 to 100 mV s^{-1}	0.72	11
Hierarchical porous carbon nanofibers	6 M KOH	1 to 10	0.68	12
Holey graphene	6 M KOH	1 to 10	0.63	13
Porous carbon monolith	6 M KOH	2 to 10	0.71	14
HPCF4	**6 M KOH**	**2 to 10**	**0.74**	**This work**
		2 to 100	**0.62**	

Table S3. Comparison of electrochemical performance of carbon-based materials in three-electrode systems.

Carbon precursor	Activating agent	C_{sp} (F g^{-1})	Current density or scan rate	electrolyte	Ref.
ZIF-8/PFA	No activation	161.0	5 mV s^{-1}	1 M H_2SO_4	15
ZIF-8	No activation	130.0	50 mV s^{-1}	0.5 M H_2SO_4	16
ZIF-8	No activation	170.0	1 mV s^{-1}	6 M KOH	17
ZIF-67	HF	238.0	20 mV s^{-1}	1 M H_2SO_4	18
ZIF-8/GO	KOH	150.0	10 A g^{-1}	1 M KOH	19
ZIF-8/PVP	HF	208	20 mV s^{-1}	1 M H_2SO_4	20
MOF-74	KOH	164	10 mV s^{-1}	1 M H_2SO_4	21
ZIF-8/MWCNT	No activation	298	10 A g^{-1}	1 M H_2SO_4	22
ZIF-8	No activation	332	0.5 A g^{-1}	6 M KOH	23
PAN/PVP/SiO_2	No activation	120	5 A g^{-1}	1 M H_2SO_4	24
HKUST-1	No activation	114.7	250 mA g^{-1}	6 M KOH	25
Silk/GO	No activation	196	300 mV s^{-1}	6 M KOH	26
GO/CNT	No activation	151.2	1 A g^{-1}	1 M H_2SO_4	27
Cotton	Sodium metal	175.1	1 A g^{-1}	1 M H_2SO_4	28
	KOH	140.0	1 A g^{-1}	1 M H_2SO4	
Melamine resin	KOH	192.7	10 mV s^{-1}	3 M KOH	29
Pilyannile	KOH	100~150	10 A g^{-1}	1 M Na_2SO_4	30
Lignin gel	CO_2	102.3	5 mV s^{-1}	6 M KOH	31
	KOH	91.7	5 mV s^{-1}	6 M KOH	
Broad beams	KOH	129.1	10 A g^{-1}	6 M KOH	32
HKSUT-1/CNT	**No activation**	**381.2**	**5 mV s^{-1}**	**6 M KOH**	**This work**
		309.1	**10 mV^{-1}**		
		259.9	**200 mV s^{-1}**		
		194.8	**2 A g^{-1}**		
		144.2	**10 A g^{-1}**		

Table S4. Specific capacitance of HPCFs and PCF4 at different scan rates.

Sample / Scan rates (mV s^{-1})	HPCF1	HPCF2	HPCF3	HPCF4	HPCF5	PCF4
5	177.4	249.4	356.1	381.2	323.7	215.8
10	118.1	230.5	271.8	309.1	289.7	209.7
20	92.9	217.7	249.7	295.2	277.7	212.3
50	77.6	205.1	231.8	272.3	265.5	200.1
100	82.5	201.6	222.9	261.4	257.9	190.2
150	66.3	195.6	217.4	257.2	250.7	180.6
200	63.9	192.9	213.8	253.9	248.0	172.9

Table S5. Specific capacitance of HPCFs and PCF4 at different current densities.

Sample / Current density (A g^{-1})	HPCF1	HPCF2	HPCF3	HPCF4	HPCF5	PCF4
2	54.1	104.9	159.9	264.8	178.6	153.2
5	37.5	94.9	129.1	160.8	144.2	142.2
10	32.0	81.9	117.3	144.2	133.3	131.3
20	28.4	79.2	111.9	129.8	130.0	121.2
30	--	77.4	108.3	127.1	124.0	112.2
40	--	73.6	106.4	123.4	121.7	108.8
50	--	71.2	99.7	125.3	122.6	99.8
100	--	69.9	97.8	120.9	117.9	75.1

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