Amidoxime-functionized Macroporous Carbon Self-Refreshed Electrode Materials for Rapid and High-capacity Removal of Heavy Metal from Water

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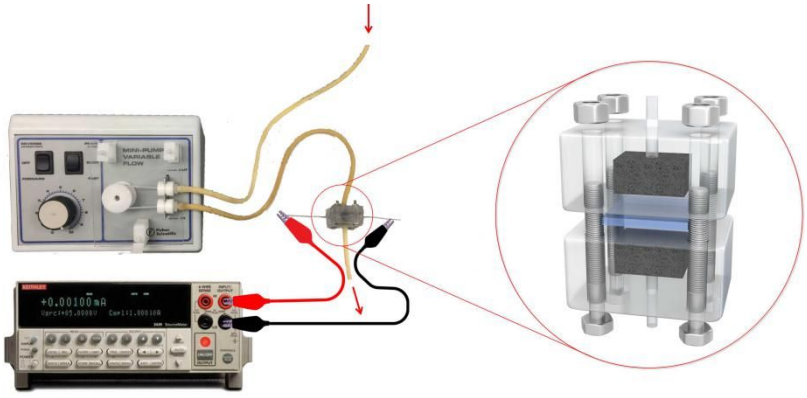

Figure S1. The demo of the filtration device setup and the detail. The kiethley instrument provide the voltage on the cell-filtration device. The peristaltic pump controls the contaminated water loading rate.

The way to get the activated materials mass loading is according to this formula:

$$M=M_3-M_1-(M_2-M_1)/2$$

M_1 is the weight of carbon felt. M_2 is the weight after coated slurry(Super P and PAN). M_3 is the weight after reaction.

Than we can get the capacity of this polymer:

$$E=(C_0-C_x)\times V/M$$

C_0 is the concentration of the original contaminated water. C_x is the concentration after deposition at that time. V means the current volume in the container. So that we can realize the filtration capability clearly from the curve in the Figure S2.

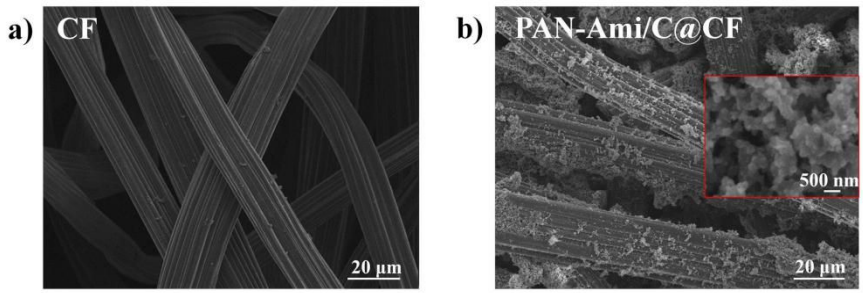

Figure S2. SEM image of carbon fiber. a) Commercial carbon felt. b), PAN-Ami/C coated carbon felt. The insert image shows the ~50nm carbon black nano particles are bound on the fiber surface with help of polymer film.

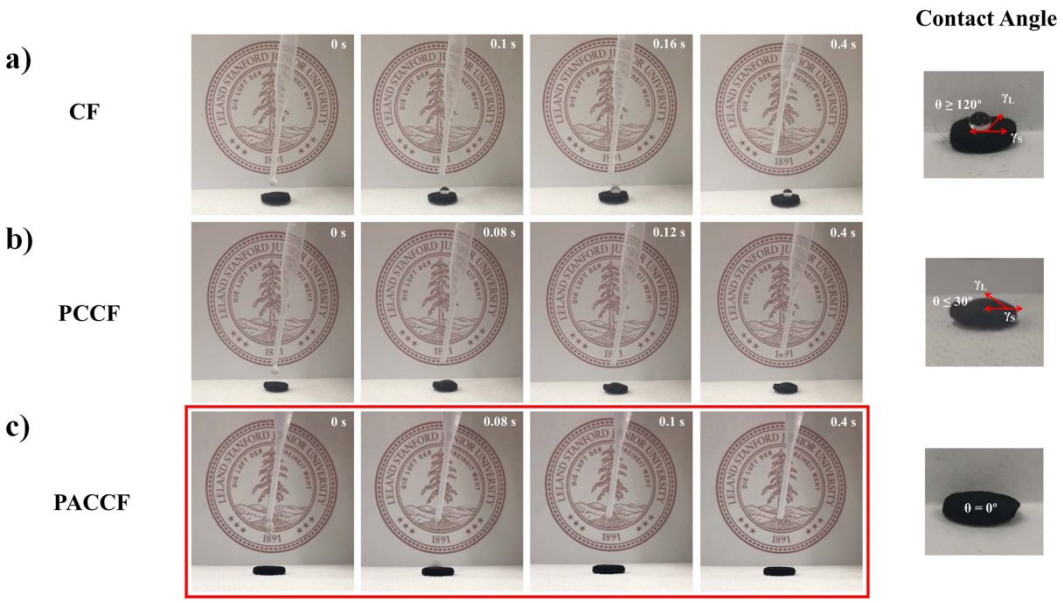

Figure S3. The hydrophilia comparison between three different materials. a) Commercial CF, the contact angle is over 120°. b) PCCF, the contact angle is less than 30°. c) PACCF. the droplet instantly soaked into the material.

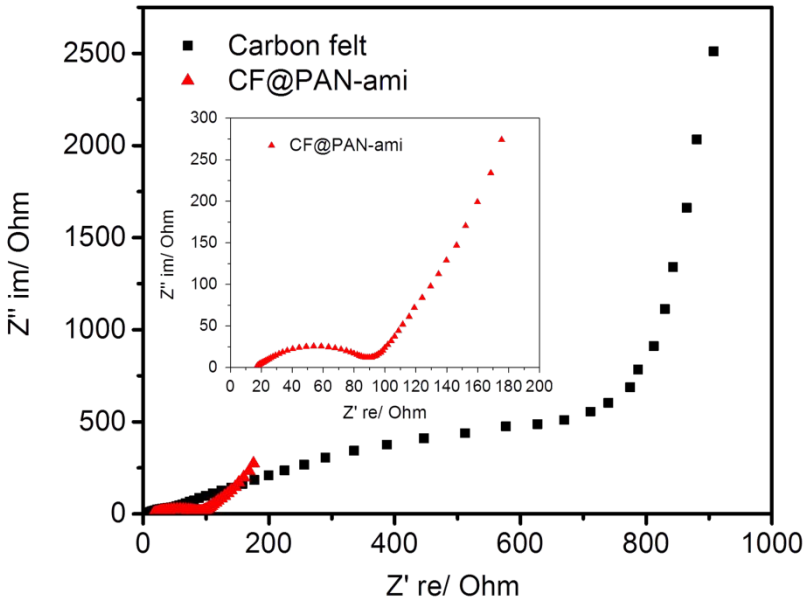

Figure S4. The electrical impedances of CF and coated CF. The black dots are the CF, the red dots are PACCF. All the tests used 0.1 M Na_2SO_4 as electrolyte.

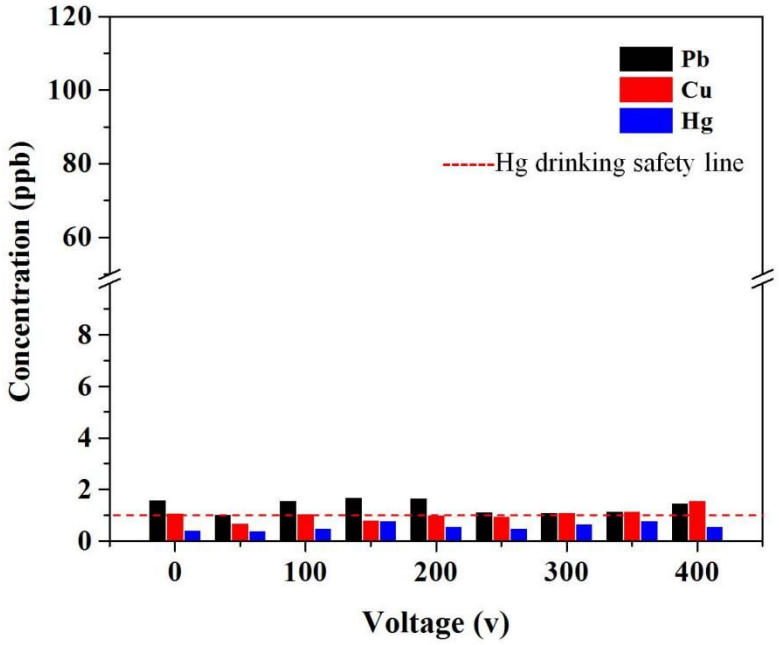

Figure S5. Flow test of Hg^{2+} removal under long term running.

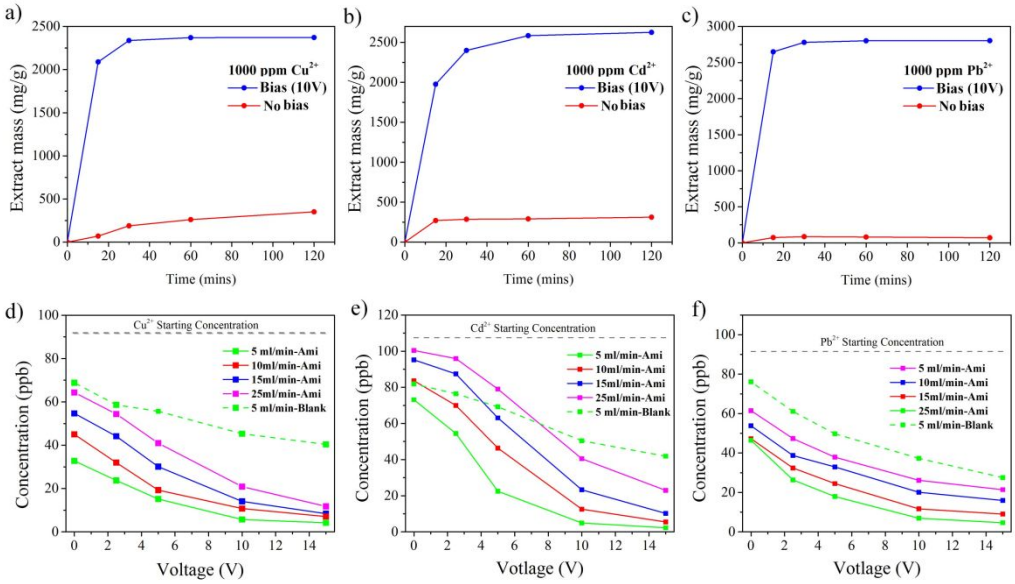

Figure S6. a), b) and c) are capacity tests of PACCF under bias and no bias in the stirring system dealing with 1000 ppm Pb^{2+}, Cd^{2+}, Cu^{2+} contaminated water, respectively (The electrode size is 1 $cm^2 \times 3.18$ cm. The polymer loading weights are 5.9 mg, 5.5 mg and 5.8 mg.). d), e) and f) are optimization tests of 100ppb single-ion simulated water by the flowing device dealing with 100 ppb Pb^{2+}, Cd^{2+}, Cu^{2+} contaminated water, respectively. The red dashes show the safe levels for each cation.

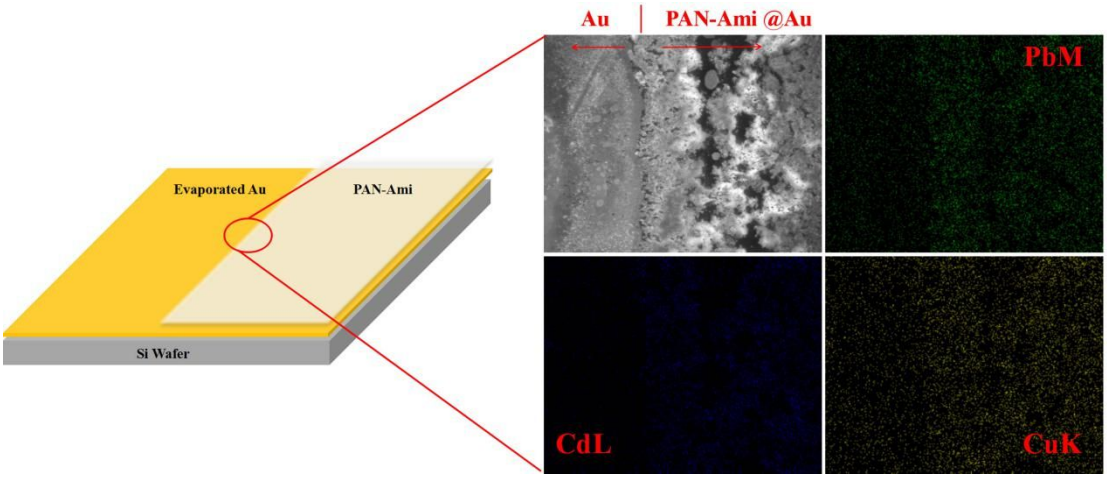

Figure S7. EDX images of the deposit on the boundary between polymer coated area and blank area under 10 V.

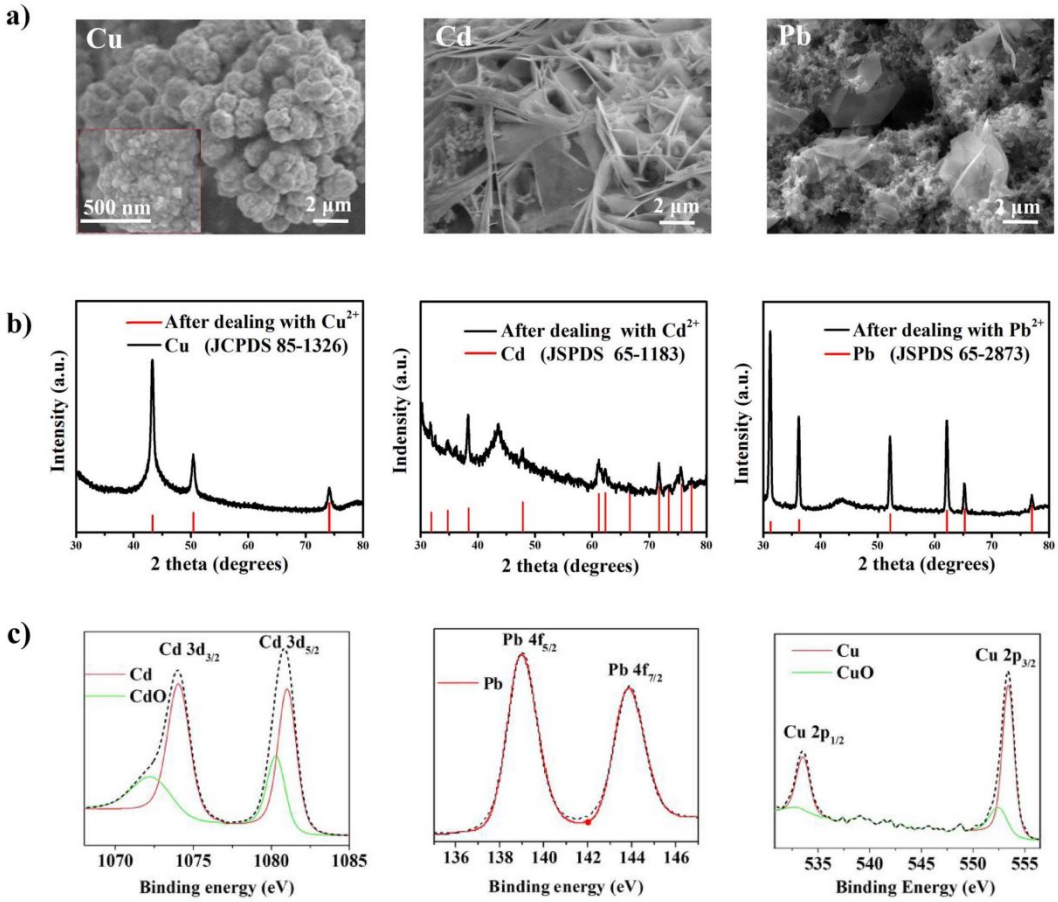

Figure S8. The removal for stirring system with 1000 ppm of single element (Cu^{2+},Cd^{2+}, Pb^{2+}) simulated water. Each concentration of residue is under the drinking safety level. a) The SEM of these three kinds of deposition covered on the electrodes after 5 min. The inset SEM of Cu shows their assembling cubic structure. b) The XRD of the deposition according to the samples in a) respectively. c) The XPS of the deposition according to the samples in a) respectively.

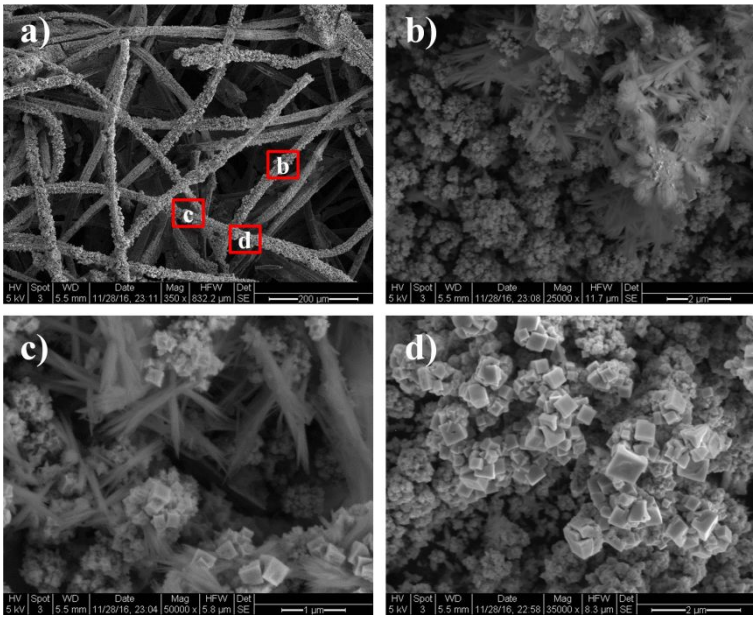

Figure S9. The removal for long term flowing with single element (Cu^{2+},Cd^{2+}, Pb^{2+}) simulated water. a) The SEM of depositions on the fibers after filtrating 3 days. Respectively, b), c), d) figures show the different nanostructures of heavy metals located on three areas, like cubic structure of Cu and flower-like flake shapes of Cd and Pb.

As we know, each metal ion has its own reduction potential in the same electrochemical working condition. These potential gaps can be used to separate the different metal. So this attempt had been applied in large concentration contaminated water (1000 ppm). In such high concentration, using alternating current instead of direct current can limit the hydrogen evolution and prevent all the ions deposit as hydroxide. Here square-wave alternating current had been applied in 100 Hz. Their reduction potentials are +0.34V (Cu^{2+}/Cu), −0.13 V (Pb^{2+}/Pb) and −0.40 V (Cd^{2+}/Cd) versus SHE (pH=0), respectively. The pH of our simulated water was around 6, so that the reduction potential of hydrogen here was around −0.35 V according to the Nernst equation. Theoretically, the metal ions can be taken out one by one under step-up voltage. But in real experiment, the Cu and Pb were always taken out together. Then the strategy changed the Pb and Cu ions were extracted first as metal in a low voltage (+3.3 V), and switch to the high voltage (1.2 V) to oxidize the Pb (to form PbO_2) and solve the Cu. After 5 hours, over 99% Pb ions had been taken out alone. (−0 V, 4.2 V) voltage was applied to attract the Cu ions, after another 5 hours operation, over 99% Cu had been deposit and less than 1% Cd ions left in the mother solution. For the remaining Cd ions, 5 V of DC was applied to rapidly collect them in 2 hours. This direct separation and recovery of heavy metal ions has great value on resources recycling comparing with traditional treatments.

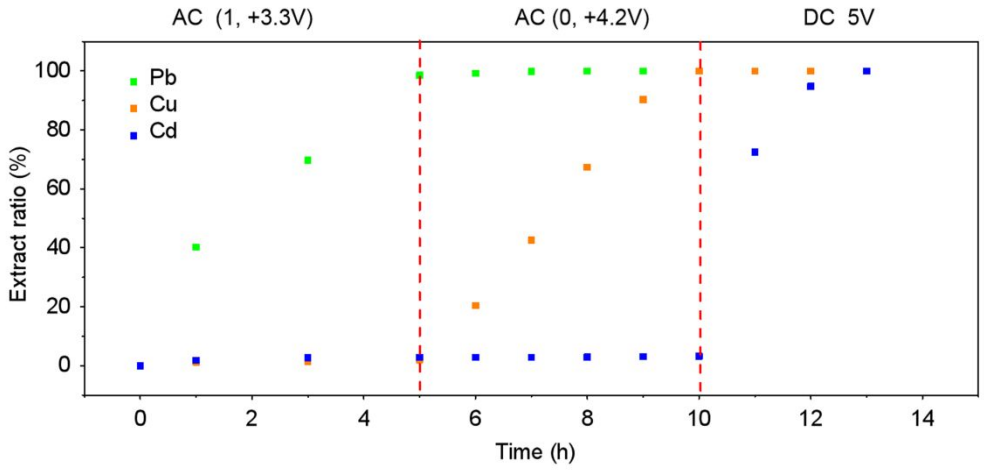

Figure S10. First, AC (1, +3.3V) applied, the Pb ions were removed by 99.99%. Then AC (0, +4.2V) applied, the Cu ions were removed by 99.99%. Last step, 5V of DC applied, the Cd ions were taken out nearly 99.99% (Origin mixture water contained 1000 ppm of Cu^{2+}, Cd^{2+}, Pb^{2+} ions each, the frequency of AC was 100 Hz).

Note 1. Power Consumption Analysis:

Unlike other pollutants adsorbents,[1-16] the energy consumption mainly generated by applying direct current on the device. So it's necessary to summarize the rough number of cost which can prove it worth to use or not.

The price of electricity used was 4~10 ¢ /kWh in most area of US.

Highest cost:

$$C_{max} = \$\ 0.10 \times 10^{-3} \times V \times I_{max} \times 1\ h \times 1000\ kg / 0.3\ kg = \$\ 6.67 \times 10^{-3}$$

Lowest cost:

$$C_{min} = \$\ 0.04 \times 10^{-3} \times V \times I_{min} \times 1\ h \times 1000\ kg / 0.3\ kg = \$\ 1.33 \times 10^{-3}$$

In the flow device tests with a small piece of materials (1 cm^2×3.18 cm), the voltage used was 10 V. In one hour, it could deal with 300 ml contaminated water (0.3 kg). The current showed was 1~2 mA. So we can get the maximum and minimum cost according to the formula above. The price of electricity in different state can really change the cost a lot. But the base line of electric charge were extremely low.

Table S1.

DFT calculation of binding energy between metals and different monomers.[a]

	Cu^{2+} (eV)	Cd^{2+} (eV)	Pb^{2+} (eV)
Amidoxime	66.81	61.96	59.61
Nitrile	6.74	16.56	12.94
Acylamino	9.09	8.14	6.32
Fluoride	11.30	6.30	5.56

[a] Values are calculated based on coordination modes reported before.

Table S2.

Performance comparison of other methods before with ours.

Adsorbents	Capacity mg/g			Efficiency (Initial C_0) % (ppm)			Current density A/m^2	Flow rate L/h	PH	Ref.
	Cu	Cd	Pb	Cu	Cd	Pb				
Electroextraction with resins		1.8			>87.5 (40)		2	0.09	-	17
Palm shell activated carbon	7.1	-	23.1	88.8 (50)	-	96.8 (50)	0.1	0.5	5	18
LMOF-263	-	7.0	18.7	-	30 (10)	80 (10)	-	-	-	19
Fe_3O_4/HA	46.3	50.4	92.4		> 95 (0.1)		-	-	6	20
Lime and Na_2S		-		-	95	-	-	-	8.5	21
Few-layered GO nanosheets/HA	-	163	-	-	50	-	-	-	6	22
Graphene-c-MWCNT hybrid aerogel	33.8	-	104.9	-	-	-	-	-	-	23
Electric driven 3D-GMOs	3820	882	434		> 96.0 (100)		-	-	2	24
Electrospun APAN nanofiber mats	150.6	-	60.6	90.5 (200)	-	97.0 (200)	-	-	4	25
This work	2300	2600	2800		> 99.9 (1000) > 95.0 (0.1)		- 0.001	- 0.3	6	-

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