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Polyaniline Nanofiber Electrodes for Reversible Capture and Release of Mercury(II) from Water

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ABSTRACT: π-Conjugated polyaniline nanofiber networks are an attractive material platform for reversible and selective capture and release of toxic heavy metal ions from water. Their nanofiber geometry facilitates high sorption kinetics, sulfur functionalization of the backbone for improved adsorption, and electrochemical control of the oxidation (charge) state for reversible triggered sorption/desorption of metal ions. These active materials also function as sensors in that the sorption of mercury ions can be detected by analysis of cyclic voltammograms. Calculation of binding energies between polyaniline and metal ions using molecular dynamics and density functional theory support the electrochemically controlled reversible sorption/desorption mechanism. These redox active materials for removing Hg²⁺ from water create an attractive system that combines efficiency, capacity, selectivity, and reusability.

INTRODUCTION

Mercury (Hg) pollution and poisoning cause serious human diseases such as the Minamata disease, and have long been a major threat to human health. In spite of this recognition, Hg ion pollution is growing world-wide from expanded manufacturing and processing of chemicals, electronic materials, and petroleum.¹ Additionally, Hg²⁺, which has long been dormant in arctic ice, is being released into the environment as a result of global warming.² Hg²⁺ pollution in drinking water is becoming a critical issue. Therefore, there is an urgent need to develop efficient technologies that can remove Hg²⁺ from polluted water to concentrations less than 2 ppb, and hence meet drinkable water standards.³

Among existing Hg²⁺ mitigation methods, adsorption as a separation method is the most facile, convenient, and practical technology.⁴ It has proven cost-effective and can have high uptake capacity, fast kinetics, and good selectivity. If the adsorption materials are stable in water over a wide pH range, the Hg²⁺ can be removed, allowing for reuse. Traditional adsorption methods include use of clay, activated carbons, zeolites, and ion exchange resins, which are often thiol-functionalized to enhance performance.⁵⁻⁷ However, the uptake capacities and binding affinities of most materials struggle to meet the necessary high standards for drinkable water.⁸⁻¹¹

Recent advances in Hg²⁺ adsorbent materials addressing this challenge include the use of highly porous organic polymers,¹²⁻¹⁴ metal–organic frameworks (MOFs),¹⁵⁻¹⁷ and covalent–organic frameworks (COFs).¹⁸⁻²¹ The enhanced adsorption using these adsorbents over traditional materials is attributed to their high surface area. MOFs have further displayed luminescence Hg²⁺ sensing capabilities, however this system has limited instability in aqueous solutions at low pH needed for regeneration.¹⁶ COFs showed increased stability, fast kinetics, and high uptake capacity, however cumbersome chemical treatments are required to enable reuse. From the economic perspective, the reuse of adsorbents is critical for real-world applications. Most often adsorbents are recycled through demetalation using strong acid¹²,²² or base,¹⁸ sometimes at elevated temperatures (70 °C).²³ Limitations associated with present-day methods include potential safety issues associated with manipulations, extra treatment steps, and limited regeneration yields. Numerous adsorbents have been developed with simple and effective chemistry, however, systems simultaneously achieving low cost, high uptake, fast kinetics, selectivity, long-term usability, and facile recyclability, remain elusive. As a result, there remains a need for new materials and methods for Hg²⁺ removal.

Electrochemically mediated capture and release of contaminants is attractive for the creation of systems that can be actuated without reagents.²⁴,²⁵ Hence we have targeted the creation of high-performance redox-active selective sorption materials that display facile regeneration by simple application of an electrical potential. These systems were also designed to compare favorably relative to existing systems in terms of water economy and downstream waste sustainability. The electrical transport properties of conducting polymers enable both the efficient charging and discharging of bulk membrane materials and the modulation of the binding of ions. The control of polymer morphologies is known to be critical for the formation of conducting polymer adsorbents for the removal of metal cations.²⁶⁻³¹ Polyaniline (PANI) is an especially notable material for this application, as a result of its facile synthesis, environmental stability, and simple doping/dedoping chemistry, the latter of which can be sensitive to its chemical environment.²⁶⁻³¹ As a result of the nitrogen groups in PANI, it naturally absorbs metal cations in its neutral state, but when oxidized its highly positively charged nature is expected to repel the cations to give a release mechanism.

RESULTS AND DISCUSSION
Preparation of polyaniline nanofiber electrodes. We demonstrate herein a working electrode of PANI nanofibers that can selectively adsorb Hg\textsuperscript{2+} from water, then subsequently release these ions upon application of an oxidizing electrochemical potential. Nanoscale PANI fibers provide high interfacial area to enhance transport kinetics of ions.\textsuperscript{32,33} These nanofibers are produced by an interfacial polymerization method using ammonium persulfate as an oxidant and camphorsulfonic acid to give polymer filaments of ca. 80 nm diameter (Fig. 1a, S1).\textsuperscript{34} Fibrous polypropylene substrates (thickness: 0.285 ± 0.05 mm, n=5) were used as the supports, and were immersed directly in the PANI synthesis solution.\textsuperscript{35} Upon contact, strong van der Waals forces result in tight binding of the PANI nanofibers to the polypropylene. Coating of nanomaterials on an economical porous substrate is a proven approach for the construction of lightweight, flexible and functional materials.\textsuperscript{36} A scanning electron microscope (SEM) image shows conformal coating of a percolated network of PANI nanofibers on the substrate (Fig. S1e), and mass of the active materials increased linearly with each dipping cycles (Fig. S2). Single dipping coated 0.83 ± 0.084 mg (n=5) of polyaniline per unit area (cm\textsuperscript{2}) of the substrate and samples from single dipping were used for further experiments. Finally, a graphite sheet was used to establish electrical contact to create a polyaniline nanofiber working electrode (denoted as PNE) with an active area of 1.5 cm\textsuperscript{2} (Fig. 1b-d, and S1d, f).

Cyclic voltammograms were recorded in 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte solution at a scan rate of 10 mV/s with pyrolytic graphite sheet as a counter electrode. Cyclic voltammograms of PNE (Fig. 1e, S3) display two characteristic peaks (0.36 and 0.94 V) in the oxidation scans, and two reduction peaks (0.88 and 0.22 V) with other processes providing small shoulders in between. The first oxidation peak corresponds to the oxidization of leucoemeraldine to emeraldine, and the second maximum at the higher potential is attributed to the oxidization of emeraldine to pernigraniline. PNEs showed very stable cyclic voltammetry profiles even after the 15\textsuperscript{th} repetitive scan cycles, and are indicative of a tight binding between the nanofibers and the substrates (Fig. S3). This aspect is important, because often electrochemically active electrodes prepared by drop casting of active materials on carbon (or general graphite) electrode, suffer from unstable long-term performance, which is generally attributed to delamination of the active materials.

Figure 1. a; Transmission electron microscopy image of PANI nanofibers. b-d; Photographic images of polypropylene support, PANI-coated absorbent, polyaniline nanofiber electrode (PNE), respectively. A 1 cm scale bar for (b-d) is placed between (c) and (d). e; Representation of deprotonated PANI and its cyclic voltammogram. f; Drawing showing the addition of mercaptopropionic acid into the PANI backbone and its cyclic voltammogram. The numbers in the cyclic voltammogram represent scan cycles after the addition of the reagent. Cyclic voltammograms were recorded in 0.5 M H\textsubscript{2}SO\textsubscript{4} electrolyte solution at a scan rate of 10 mV/s with pyrolytic graphite sheet as a counter electrode.
In its oxidized state, polyaniline becomes acidic and can be readily deprotonated. Repetitive anodic scans in basic pyridine solutions deprotonate the PANI backbone to create very electrophilic alkenes flanked by imines poised for conjugate addition chemical reactions with thiols. Cyclic voltammetry with pyridine (37 mmol) resulted in a gradual current decrease with increasing scans (Fig. 1e). This behavior is expected as PANI becomes electrochemically inactive with deprotonation, which is accomplished in 9 anodic scans. We then added 3-mercaptopropionic acid (11 mmol) with continued electrochemical cycling, to functionalize the PANI backbone via a new S-C linkage. The 3-mercaptopropionic acid provides an additional chelating group for the removal of heavy metal ions to the electrochemically active conducting network. Following the addition of 3-mercaptopropionic acid the film regains its electroactivity (Fig. 1f). The voltammogram gained intensity through the 9th sweep, and PANI with additional sulfur-containing chelating groups are denoted as PNE-S (mass gained after S-functionalization: 0.064 ± 0.000065 mg/cm², n=5).

We confirmed the successful grafting of the mercaptopropionic acid groups to the PANI nanofibers by Fourier transform infrared spectroscopy (FTIR) and X-ray photoelectron spectroscopy (XPS) studies. The FTIR spectra of PNE showed all major peaks from PANI including C-N stretching vibration (quinoid unit) at 1567 cm⁻¹, C=C stretching vibration (benzenoid unit) at 1484 cm⁻¹, C-N stretching mode of benzoid ring at 1298 cm⁻¹, aromatic C-H in plane bending vibration at 1131 cm⁻¹, and C-H out of plane bending vibration at 810 cm⁻¹ (Fig. S4). The PNE-S had two new peaks: one sharp peak at 1690 cm⁻¹ assigned to a C=O stretching vibration from carboxylic acid, and another broad peak 3300-2500 cm⁻¹ (centered at 3000 cm⁻¹) for the carboxylic acid O-H stretching vibration. The XPS spectra of PNE-S indicated the appearance of a sulfur signal at an electron binding energy of 163.2 eV, which is consistent with ionization of the S(2p) orbital of the thiol group (Fig. S5). We confirmed that PANI displays its maximum Hg²⁺ adsorption performance at pH ranges from 4 to 6 (Fig. S6). Thus, for all adsorption experiments, we fixed the pH value at 5.8, unless otherwise mentioned.

**Performance of PNE-S: Recyclability, selectivity, and sensibility.** For analysis of the reversible removal and release of Hg²⁺, PNE-S was soaked in 10 mL 1000 ppb Hg²⁺ solution for 12 h, removing 99.8% of Hg²⁺ from the solution as determined by inductively coupled plasma mass spectrometry (Fig. 2a). Subsequent application of oxidizing potential (0.5 V) for 45 min released 82% of the initially adsorbed Hg²⁺. Following that, the electrode was reduced for 10 min with 0.1 V in a fresh electrolyte solution. On the second cycle, the PNE-S removed 81% of Hg²⁺ out of another fresh 1000 ppb 10 mL solution. Subsequent oxidation released 95.6% of the Hg²⁺ based on the second cycle. Notably, release rate for a third cycle increased to 97.8%. About 18% of the absorbed Hg²⁺ is not released from the electrode that was absorbed on the first cycle, presumably because Hg²⁺ is occupying preferred strong binding sites. Because the Hg²⁺ release experiments are per-
formed with oxidizing potential we do not expect Hg$^{2+}$ to be reduced to Hg$^0$ or Hg$^0$ forms. Mercury ion binding to the sulfur groups was confirmed by XPS. Upon the adsorption, electron binding energy of sulfur is upshifted to 164.8 eV, caused by donation of electrons from sulfur atoms to mercury ions (Fig. S5). Selectivity is an important factor for practical heavy metal ion removal from water that is likely to contain a variety of ions. For this, we soaked PNE-S in 40 mL solution containing different metal ions (5 mL each of 1000 ppb Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, and K$^+$. PNE-S displays relatively good selectivity for toxic metals, removing greater than 99 % of the Hg$^{2+}$, along with a large fraction of Pb$^{2+}$ (67%) and Cd$^{2+}$ (24%). Interestingly, PNE-S is inactive toward Zn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, and K$^+$ (Fig. 2b). Unfunctionalized PNE showed slightly increased selectivity towards Hg$^{2+}$, removing 90% of it along with a small amount of Pb$^{2+}$ (22%) and Cd$^{2+}$ (15%), and also inactive for the rest of the ions (Fig. S7). It is noteworthy that PNE-S has even greater selectivity for Hg$^{2+}$ over PNE.

We find that Hg$^{2+}$ absorption/release is accompanied by changes in the cyclic voltammograms. PNE-S fully loaded with Hg$^{2+}$ (PNE-S was soaked in 10 mL 1000ppb Hg$^{2+}$ solution overnight) is electrochemically inactive as indicated by the voltammogram at t = 0 min (Fig. 2c, d). To release Hg$^{2+}$, a fixed potential of +0.5 V was applied. After 2 min, the fixed potential was removed, and cyclic voltammetry between 0.0 and +0.8 V (scan rate of 10 mV/s) of PNE-S was recorded. Immediately after the cyclic voltammetry, application of 0.5 V fixed potential was continued until the next cyclic voltammetry measurement. In this manner, the sequential voltammograms at t = 5, 20, and 40 min were further obtained (Fig. 2d). As the adsorbed ions are removed from the PNE-S, it recovers its native electrochemical activity. We also performed another set of experiments to show the relationship of the cyclic voltammogram and adsorbed ion. For this, we soaked PNE-S in its reduced form into a vessel of 20 mL of 1000 ppb Hg$^{2+}$ solution to adsorb the ions. Immediately upon addition to the solution, a cyclic voltammetry between 0.0 and +1.0 V was recorded (t = 0), showing redox peaks with quite strong current density (Fig. S8). Cyclic voltammograms at t = 2, 4, 8, 10, 30, 45, and 60 min were then further obtained with no potential being applied between cycles. As Hg$^{2+}$ are adsorbed onto the PNE-S, the electrochemically activity declines.Voltammogram profiles depend upon the sorption state of Hg$^{2+}$ and the two sets of experiments mutually corroborate each other, proving the electrode’s potential utility as an active sensing material.

**Calculation of intermolecular binding energies of polyaniline and metal cation complexes.** To provide a molecular-level understanding of the binding characters between different oxidation states of PANI model geometry and various metal ions (M$^{n+}$ = Hg$^{2+}$, Pb$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Ca$^{2+}$, Mg$^{2+}$, and K$^+$), we performed molecular dynamics (MD) simulations, density functional theory (DFT) calculations and hybrid quantum mechanics/molecular mechanics (QM/MM) calculations on PANI-M$^{n+}$ complexes in select aqueous solutions. These results decipher the adsorption mechanisms and the effects of electrochemical modulation. We restricted the present study to model PANI structure without additional sulfur functional groups, in order to show binding contribution from pure PANI. Three PANI tetramers, with neutral charge, oxidized by losing one and two electrons, are denoted as PANI(0), PANI(I) and PANI(II), and tested (Fig. S9). Starting with geometries of PANI-M$^{n+}$ complexes optimized from gas-phase DFT calculations, we sampled their binding configurations in the solution phase using MD. Based on the snapshots of these MD trajectories, the binding energies ($E_{bind}$) of all these PANI-M$^{n+}$ complexes were evaluated with the presence of explicit water molecules using QM/MM (Table S1, and Fig. S10, S11):

$$E_{bind}(M^{n+}) = E(PANI) + E(M^{n+}) - E(PANI - M^{n+})$$

**Figure 3.** Intermolecular binding energies of polyaniline and metal cation complexes were sampled in aqueous solutions using MD simulations, and evaluated using CDFT and QM/MM approaches. (See SI for the computational details.)

In agreement with experimental observations, all metal ions are statistically bound to the reduced state of PANI ($E_{bind} > 0$ for PANI(0), Fig. 3). Among these ions, Hg$^{2+}$ exhibits the greatest binding strength ($9.5 \pm 13.9$ kcal mol$^{-1}$), followed by Pb$^{2+}$ and Cd$^{2+}$ ($3.0 \pm 14.4$ kcal mol$^{-1}$ and $3.2 \pm 13.1$ kcal mol$^{-1}$, respectively), while other ions are bound more loosely. The binding preference of PANI towards heavy Hg$^{2+}$ is the result of strong dispersion and polarization contributions to the van der Waals forces. In addition, assuming Maxwell–Boltzmann statistics are completely reached at room temperature, $E_{bind} (Hg^{2+}) = 9.5$ kcal mol$^{-1}$, corresponding to the only 10$^{-2}$ % of Hg$^{2+}$ remaining in the aqueous solution at equilibrium. The deviation between theory and experiment is probably due to the existence of an interaction barrier on the magnitude of a few kcal mol$^{-1}$. On the other hand, oxidized PANI released the adsorbed metal ions as a result of increasing electrostatic repulsion between the two entities. The release was confirmed by negative values of $E_{bind} (Hg^{2+}) < -25.5 \pm 21.1$ kcal mol$^{-1}$ and $-72.4 \pm 23.5$ kcal mol$^{-1}$, for PANI(I) and PANI(II), respectively. Among these ions, K$^+$ has a single positive charge while the others are dicationic, and therefore K$^+$ shows the smallest electrostatic repulsion with oxidized PANI species. Our MD simulations and QM/MM calculations provides theoretical evidence to support the construction of electrochemically active materials for the removal of charged species. These phenomena have never been deeply investigated in earlier studies.

**Adsorption behaviors of polyaniline nanofiber electrodes.** Besides the unique recycle and sensing mechanisms, we also analyzed two indicators of adsorbents’ performance: kinetics (how fast adsorbates can be removed) and isotherms
(how much adsorbates can be removed). For kinetic measurements, electrode samples (1.27 and 1.37 mg for PNE and PNE-S, respectively) were soaked in 1 ppm solution of Hg(NO$_3$)$_2$ (10.0 mL) for different lengths of time. PNE-S removed more than 98% of Hg$^{2+}$ in 10 min (Fig. 4a). Kinetic equilibrium was reached after 150 min, and the 1000 ppb solution was reduced to 1.8 ppb, which satisfies the U.S. Environmental Protection Agency (EPA) standard (< 2 ppb) for drinking water. PNE showed a slightly slower response, removing 74% of initial Hg$^{2+}$ in 10 min. After 150 min, ca. 10% (103 ppb) of Hg$^{2+}$ were still left unbound. The adsorption process consists of two steps (Fig. 4a-c): a rapid primary step and a slow secondary step. The rapid step is attributable to physical ion-exchange adsorption of Hg$^{2+}$ to the polymer surface. Meanwhile, the slow step likely involves diffusion of Hg$^{2+}$ ions to the interior of the polymer nanofibrils.

The chemical interactions, especially the formation of the coordination or chelation bonds between electron-rich nitrogen and sulfur atoms, and electron-deficient mercury ions, are involved in the rate-determining step. Thus, we employed a pseudo-second-order chemical reaction kinetic model to extract rate constants of the materials using the following equation:

$$\frac{t}{q_t} = \frac{1}{k_2q_e^2} + \frac{t}{q_e}$$  \hspace{1cm} (Eq. 2)

$q_t$, $q_e$ (mg g$^{-1}$) are the amount of mercury ion adsorbed (mg g$^{-1}$) at time $t$ and equilibrium (min), respectively, and $k_2$ (g mg$^{-1}$ min$^{-1}$) is the rate constant of the model. The $t/q_t$ versus $t$ relation (Fig. 4b inset) was found to be linear with an $R^2$ value of 1 for both electrodes, meaning that the second order model is applicable. Our electrode samples have rate constants of 3.80 x 10$^3$ g mg$^{-1}$ min$^{-1}$ and 4.37 x 10$^3$ g mg$^{-1}$ min$^{-1}$ for PNE-S and PNE, respectively. Notably, these rate constants are 2-3 orders of magnitude higher than those of other PANI adsorbents under similar conditions (Table S2). It is reasonable to assume that the faster kinetics are related to the large surface area within the PNEEs and PNE, facilitating the diffusion of Hg$^{2+}$ into the chelating atoms. We attempted to correlate the experimental data to a physisorption dominant pseudo-first-order kinetic model (Fig. S12). However, the much lower correlation coefficients ($R^2$ for PNE-S and PNE are 0.77 and 0.92, respectively) from this model proved that the chemisorption is the dominant sorption kinetic.

Sorbent's affinity for a target metal ion is another important aspect of adsorbents and is represented by their mass-weighted distribution coefficient, $K_d$. $K_d$ is defined as

$$K_d = \frac{C_i - C_f}{V} \times \frac{C_f}{m}$$  \hspace{1cm} (Eq. 3)

where $C_i$ is the initial metal ion concentration, $C_f$ is the final equilibrium metal ion concentration, $V$ is the volume of the treated solution (mL), and $m$ is the mass of sorbent used (g). $K_d$ values of 1.0 x 10$^5$ mL g$^{-1}$ are usually considered excellent. PNE-S had an exceptional $K_d$ value of 4.39 x 10$^6$ mL g$^{-1}$, and PNE had a fairly high value of 6.77 x 10$^5$ mL g$^{-1}$. This is one of the highest values reported thus far for PANI based adsorbents. Only a few examples of non-PANI adsorbents with high porosity had higher $K_d$ values than that of PNE-S (Table S3).

Figure 4. a, b; Kinetic studies of the electrodes: (a) Hg$^{2+}$ adsorption kinetics of the electrodes under the Hg$^{2+}$ initial concentration of 1 ppm, and (b) Adsorption capacity curve of Hg$^{2+}$ versus contact time. Inset shows a pseudo-second-order kinetic plot. c; Hg$^{2+}$ adsorption isotherm for the electrodes. Inset shows the pseudo-first-order kinetic model is applicable.
Maximum uptake capacity of the PNE-S and PNE were calculated from the adsorption isotherms over the range of Hg$^{2+}$ concentrations from 1 mg L$^{-1}$ up to 500 mg L$^{-1}$ (Fig. 4c). The equilibrium isotherm data were fitted using the Langmuir model (Eq. (4)) with which a high correlation coefficient ($>0.988$) was obtained (Fig. 4c, inset).

$$\frac{C_e}{q_e} = \frac{1}{K_L} + \frac{C_e}{q_m}$$  

(Eq. 4)

where, $C_e$ is equilibrium concentration of Hg$^{2+}$ (mg L$^{-1}$), $q_e$ is amount adsorbed under equilibrium (mg g$^{-1}$), $K_L$ is the Langmuir binding constant related to the energy of adsorption (L mg$^{-1}$), and $q_m$ is theoretical maximum adsorption capacity of the adsorbent for Hg$^{2+}$ (mg g$^{-1}$). Remarkably, PNE-S and PNE both had very high maximum mercury adsorption capacity, $q_m$. of 971 mg g$^{-1}$ and 644 mg g$^{-1}$, respectively (Fig. 4c, d). The maximum mercury uptake capacity of PNE-S is one of the highest values reported for PANI adsorbents (Table S3). Only a few highly porous networks adsorbents exhibit higher $q_m$ than that of PNE-S. Thus 971 mg g$^{-1}$ from PNE-S is an encouraging result, demonstrating sulfur functionalized mesoporous nanofibers can match the uptakes of the best nanoporous materials. The mesoporous morphology, together with a large number of highly accessible sulfur atoms, qualify PNE-S as an outstanding mercury sorption material.

**CONCLUSION AND OUTLOOK**

We demonstrated redox-active adsorbents that electrochemically control capture and release of Hg$^{2+}$. Sulfur-atom functionalized PNE-S showed significantly faster $k_2$ and higher $q_m$ than any other reported PANI adsorbents. With such high performance values, selectivity, and reusability, PNE-S is a promising Hg$^{2+}$-sensing and purification material. These results suggest that PANI nanofibers offer a powerful and economical platform for tailor-made structural design to remove environmental pollutants. Targeting different toxic ions and developing a higher capacitance ($q_m$) and faster response ($k_2$) are future directions.

**EXPERIMENTAL SECTION**

**Materials.** Aniline (ACS reagent, ≥ 99.5%), ammonium persulfate (ACS reagent, ≥ 98%), camphorsulfonic acid (≥ 98%), pyridine (≥ 99.8%) and 3-mercaptopropionic acid (≥ 99%) were purchased from Sigma-Aldrich and used as received. Freshly distilled aniline was used for experiments. All solvents used were of HPLC grade. Millipore water (18.2 MΩ·cm) was used for sample rinsing and preparation of all aqueous solutions.

**Synthesis of polyaniline nanofibers.** The interfacial polymerization reaction of aniline was performed in a 20 mL glass vial (Fig. S1a, b). 3.2 mmol amount of aniline was dissolved in 10 mL of dichloromethane. Ammonium persulfate (0.8 mmol) was dissolved in 10 mL of 1 M camphorsulfonic acid dopant solution. The water solution was carefully transferred into a vial containing the dichloromethane solution, resulting in interfacial polymerization of aniline. After overnight, the as-prepared PANI was purified by filtration to remove excess acid and byproducts.

**Preparation of polyaniline nanofiber electrodes.** The obtained nanofibers (0.25 mg) were transferred in DI water (5 mL) then sonicated for 30 min without any surfactants. The filtered as-prepared polyanilines are prone to aggregation during the drying process. Sonication was treated to re-dispersed polyanilines into their original nanoscale fibers. PANI samples prepared from one-hour sonication showed the best adsorption performance by maximizing exposure of inner functional groups. A polypropylene sheet (PIG® HazMat Handy Pad, MAT351, 10 x 30 mm$^2$) with thickness of 0.285 ± 0.05 mm was dipped into the PANI dispersion in water for 3 sec then removed to be dried in the air for 30 min. The micro/macro fibrous structure of polypropylene allows the fibers to absorb large amounts of water or other polar solvents. The interaction of polypropylene with PANI is facilitated by these properties. The samples were completely dried in 60 °C vacuum oven overnight. Fig. S2 shows the accumulated PANI mass absorbed per cm$^2$ by the polypropylene mat with different numbers of soaking times. Due to the high absorption of the substrate, the process of adsorption is quick and can be potentially easily scaled up. The prepared PANI-coated polypropylene sheet was cut into size of 10 x 18 mm$^2$. Graphite paper (Panasonic) was cut into the same size. They were sandwiched using an adhesive tape to have an overlap length of 3 mm (Fig. S1d, f). Previous studies have shown that PANI films have mesoporosity ranging ca. 30-50 m$^2$ g$^{-1}$.

**Electrochemistry.** Electrochemical studies were carried out under ambient conditions with an Autolab Model PGSTAT20 potentiostat (Eco Chemie). A three-electrode configuration consisting of the prepared electrode as the working electrode, Ag/AgCl (3 M KCl) as a reference electrode, and a pyrolytic graphite sheet as a counter electrode was used. The supporting electrolyte was 0.5 M H$_2$SO$_4$ in DI water. Deprotonation of PANI was performed by repeated potential sweeps between 0.0 and +1.0 V (scan rate of 10 mV/s) with an excess pyridine (37 mmol) at room temperature. Functionalization of the PANI was done by the same condition with 11 mmol of 3-mercaptopropionic acid added into the CV cell. After each step of electrochemistry, samples were rinsed with fresh electrolyte solution. The prepared samples were dried in the 60 °C vacuum oven overnight. All the potentials are mentioned with respect to standard normal Ag/AgCl reference electrode.

**General characterization methods.** X-ray photoelectron spectroscopy measurements were performed on a Physical Electronics VersaProII X-ray photoelectron spectrometer with a hemispherical energy analyzer and a monochromated X-ray source (Al Kα, 1486.6 eV). Scanning electron microscope analysis was performed on a JEOL JSM-6010LA. Transmission electron microscope images were obtained with a 120 kV FEI Tecnai Multipurpose TEM. Fourier transform infrared (ATR-FIR) spectra were acquired using a Thermo Scientific Nicolet 6700 FT–IR with a Ge crystal. Inductively coupled plasma mass spectrometry (ICP-MS, AGILENT 7900) was used for direct detection of ion concentration.

**Hg$^{2+}$ sorption kinetic tests.** A 10 mL aqueous Hg(NO$_3$)$_2$ (1 ppm, pH = 5.8) was added into a 20 mL glass vial. Then one electrode sample was soaked in for a desired time at room temperature with a stir bar gently stirred. After desired time, the solution was filtered through a syringe filter (VWR, 0.20 µm filter). Then, the filtrates were analyzed using ICP-MS to determine the concentration of Hg$^{2+}$.

**Hg$^{2+}$ sorption isotherm tests.** Different concentrations of a 10 mL aqueous Hg(NO$_3$)$_2$ (pH = 5.8) was added into a 20 mL glass vial. Then one electrode sample was soaked in and gently stirred for 12 h at room temperature. After the time, the solution was filtered through a 0.20 µm syringe filter. Then, the filtrates were analyzed using ICP-MS to determine the concentration of Hg$^{2+}$.

**Recycle test.** To release the Hg$^{2+}$ ions, fixed oxidizing potential 0.5 V was applied to the fully adsorbed PANI electrode up to 1 hour at room temperature, while gently stirred. Subsequently, the PANI electrode was reduced for 10 min with 0.1 V in a fresh electrolyte solution. The sample was re-soaked into another fresh 10 mL of 1000 ppb Hg$^{2+}$ solution, for the next cycle of test.

**Ion selectivity tests.** One PNE sample was soaked into an Erlenmeyer flask containing a total of 40 mL aqueous solution (5 mL each of 1000 ppb Hg(NO$_3$)$_2$, Pb(NO$_3$)$_2$, Cd(NO$_3$)$_2$, Zn(NO$_3$)$_2$,}
Cat(NO$_3$)$_3$, Mg(NO$_3$)$_2$, Ni(NO$_3$)$_2$, and KNO$_3$; pH = 5.8) for 12 h at room temperature with a stir bar gently stirred. Then, the filtrates were analyzed using ICP-MS to determine the concentrations.

ASSOCIATED CONTENT

Supporting Information. Details about materials, synthetic protocols, characterization methods, and computational studies are supplied as Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

There are no conflicts to declare.

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