Fluorescent Hydrogel-Coated Paper/Textile as Flexible Chemosensor for Visual and Wearable Mercury(II) Detection

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In some industrial districts, abuse discharge of waste water has resulted in serious Hg^{2+} pollution in seafood, grain, and even drinking water. In order to protect people from mercury(II)-polluted food and water, many solid-state fluorescent Hg^{2+}-sensing materials are developed in terms of facile operation. However, one primary challenging issue is the restricted sensitivity caused by hindered slow diffusion of aqueous testing samples inside these conventional hydrophobic, dense, and rigid film materials. Herein, robust hydrophilic fluorescent hydrogel-coated flexible paper/textile film chemosensors are reported. Their design relies on a specific chemical reaction between Hg^{2+} and the grafted thiourea moieties to induce remarkable "green-to-blue" emission color change. Thanks to their hierarchical porous structures fixed by interwoven paper/textile fibers, these flexible chemosensors allow fast capillary-force-driven mercury(II) diffusion into the hydrophilic hydrogel matrix, thus enabling visual detection of nearly nM-level Hg^{2+}. On this basis, robust fluorescent hydrogel-coated wearable sensing gloves are fabricated for the first time, which significantly facilitate infield visual detection and effectively protect operators far from the toxic Hg^{2+}-polluted samples. These developed flexible wearable sensing systems might not only hold great potential applications in mercury(II) detection, but also inspire the development of next-generation sensing apparatus for other food and environmental pollutants.

1. Introduction

As is reported, the Hg^{2+} content of environmental surface waters has tripled compared to pre-anthropogenic conditions primarily because of human activities, which results in serious Hg^{2+} pollution in seafood, grain, and even drinking water especially in many industrial districts.[1–4] Therefore, it is of great urgency to develop facile and effective sensing apparatus to discriminate Hg^{2+}-polluted food and water samples. For this purpose, a large amount of powerful electric, colorimetric, and fluorescent Hg^{2+} chemosensors have been developed over the past decades.[5–15] Nevertheless, most of these Hg^{2+}-sensing studies, despite state-of-the-art, are primarily based on solution phase. For practical infield applications, solid-state sensing materials are more attractive as they can provide operational simplicity, portability, and good stability.[16–27]

Among various solid-state sensing materials, flexible fluorescent hydrogel films are attracting increasing attention in recent years.[28–41] This is because hydrogels are hydrophilic, water swellable polymer networks that can allow efficient diffusion of water-soluble pollutants into the hydrogel matrix.[42–49] Moreover, their chemical and physical properties could be finely tuned via proper molecular design in order to further enhance their binding affinity for targeted molecules. Therefore, these flexible hydrogel chemosensors can address the restricted detection sensitivity caused by hindered and slow diffusion of aqueous testing samples inside conventional hydrophobic, dense sensing films, thus generating higher

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quality signals. For example, Serpe and co-workers reported multiresponsive microgel-based etalons that can be successfully used for facilely quantitative analysis of the nerve agent diethylcyanophosphate.[36] Tang and co-workers took advantage of the assembly of positively charged aggregation-induced emission fluorogens with poly(acrylic acid) to fabricate a robust supramolecular sensing film, which enables regional environmental RH detection, internal humidity mapping, and sensitive human-body humidity-sensing applications.[50] Recently, we have also presented two kinds of polymeric hydrogel films that enable ultrafast detection of pH[51] and ppm-level nitro aromatic pollutants[52] in aqueous media. These impressive examples suggest that flexible fluorescent hydrogel films can be quite good sensing platform for many environmental pollutants. However, such studies, despite promising and convenient, have seldom been used for the toxic Hg^{2+} detection.

On the other hand, there has also been an increasing interest in fabricating flexible paper/textile-based fluorescent sensing films because of their unique properties.[53–55] For example, the interwoven fibers of paper and textile can endow the as-prepared fluorescent sensors with hierarchical porous structures, which are favorable for the fast and spontaneous capillary force driving diffusion of aqueous testing samples.[52,55] This property is quite desired, because it can solve several challenging drawbacks of traditional rigid sensing films, especially restricted sensitivity caused by hindered diffusion of aqueous pollutant solutions inside traditional dense film materials. Additionally, due to the freestanding nature of cellulose paper and textile fiber, it is possible to generally mass produce flexible sensory films by simply in situ crosslinking the fluorescent polymers, even for those poor film-forming materials. More importantly, considering that these flexible paper/textile-based films can be low-cost, light-weight, and arbitrarily tailored, it is very promising to integrate the as-prepared film sensors into next-generation portable, safe, or even wearable sensing apparatus.[55] However, such promising studies have not yet been conducted for Hg^{2+} detection.

Herein, we present a new kind of flexible hydrophilic fluorescent hydrogel-coated paper (FHCP) film chemosensors, which enable ratiometric, visual, and even wearable detection of nearly nM-level Hg^{2+} in aqueous solutions. These flexible green-light-emitting FHCP films are fabricated by in situ crosslinking paper through radical copolymerization of Hg^{2+}-sensitive 1,8-naphthalimide-based monomer (NDBCB, see Scheme S1, Supporting Information), the 2-hydroxyethyl methacrylate (HEMA) comonomer, and N,N′-methylene bis(acrylamide) cross-linker (**Figure 1**a). The fluorescence intensity of these flexible hydrogel-coated films can be precisely controlled by varying the feed ratio. As illustrated in Figure 1a, upon exposure to aqueous Hg^{2+} solutions, the fast and spontaneous capillary force driving diffusion of Hg^{2+} solutions into hydrogel-coated film brings Hg^{2+} and the grafted thiourea moiety together, which results in desulfurization of the thiourea groups and subsequent cyclization to produce the corresponding blue-light-emitting guanidine derivatives (Figure 1b).[19] As a consequence, the highly green-light-emitting polymer hydrogel-coated paper chemosensor gradually becomes blue, generating Hg^{2+}-concentration-dependent fluorescence intensity and color change. Furthermore, in order to facilitate the infield detection

and effectively protect the operators far from the toxic Hg^{2+}-polluted samples, we develop a type of fluorescent hydrogel-coated wearable sensing gloves that display visible "green-to-blue" emission color upon touching the Hg^{2+}-polluted food samples. These developed flexible and wearable paper/textile-based fluorescent chemosensors, characterized with high sensitivity and selectivity, safe and facile operation, ratiometric and naked-eye Hg^{2+} detection properties, hold great potential for many practical applications in environmental water or food analysis.

2. Results and Discussion

2.1. Directly Coating Fluorescent Polymer Hydrogel on Filter Paper

The Hg^{2+}-responsive 1,8-naphthalimide-based NDBCB monomer was first prepared through the synthetic procedures shown in Scheme S1 (Supporting Information) and characterized by ^1H NMR spectroscopy (see Figures S1–S3, Supporting Information).[19] The NDBCB monomer exhibits poor water solubility, but is highly soluble in dimethyl sulfoxide (DMSO). As shown in Figure S4 (Supporting Information), its DMSO solution displays intense green light emission of the naphthalimide fluorogens when excited at 365 nm under a handheld UV lamp. Its exposure to Hg^{2+} will lead to desulfurization of the thiourea moieties and cyclization to produce the corresponding blue-light-emitting guanidine derivatives. As a result, a visible emission color change from green to blue was observed in NDBCB solutions upon addition of only ppm-level mercury ions, indicating that NDBCB may work as a sensitive and visual Hg^{2+} probe.

The fluorescent polymer hydrogel-coated filter paper was then fabricated by absorbing mixed DMSO solutions of NDBCB, HEMA monomers onto filter paper, and then in-situ crosslinking polymerization using N,N′-methylene bis(acrylamide) (MBAA) as cross-linker (Figure S5, Supporting Information). After being successively washed by ethanol, DMSO, and deionized (DI) water to fully remove the unreacted monomers, the hydrogel-coated paper films were dried at 60 °C. On the basis of the possible modulation of the fluorescent features, five hydrogel-coated paper samples were synthesized by varying the feed ratio of NDBCB to HEMA. Table S1 (Supporting Information) summarizes the synthetic formulation of these five samples. As expected, all of these samples emit bright green light (**Figure 2**a) under a handheld UV lamp at 365 nm, which is in sharp contrast to the nonfluorescent pristine filter paper. Their emission intensities gradually rise as the NDBCB content increases, as is evidenced by the recorded fluorescence spectra shown in Figure 2b. To further access the uniformity of the obtained fluorescent hydrogel-coated paper films, a statistical analysis was taken to measure the variations in fluorescence intensities at 501 nm from seven different spots of the films. As summarized in Figure 2c and Figure S6 (Supporting Information), excellent consistency was proved for seven different measurements, indicating the quite good photoluminescence uniformity of these paper films. Figure 2d–f compares typical scanning electron microscopy (SEM) images, Fourier transform infrared-attenuated total reflection (FTIR-ATR)
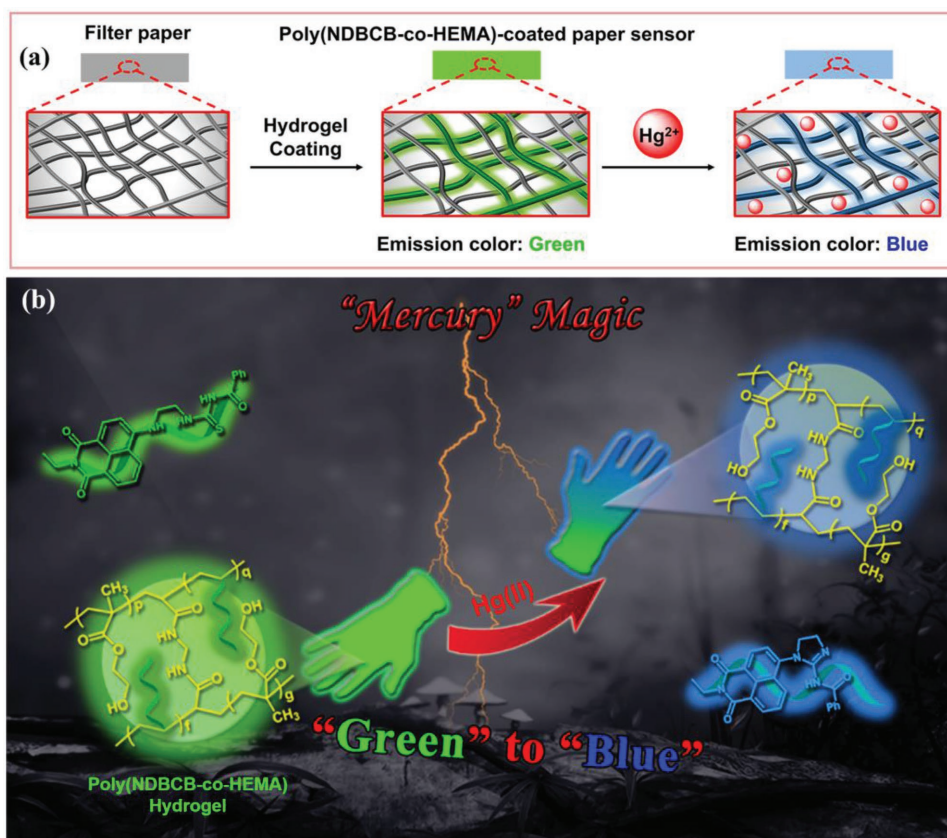
Figure 1. a) Fabrication of the fluorescent hydrogel-coated paper (FHCP) chemosensors for visual Hg^{2+} detection. These green-light-emitting FHCP chemosensors are fabricated by absorbing mixed DMSO solutions of Hg^{2+}-sensitive NDBCB monomer, 2-hydroxyethyl methacrylate (HEMA) comonomers onto filter paper, and then in situ crosslinking polymerization using N,N'-methylene bis(acrylamide) (MBAA) as cross-linker. Upon exposure to aqueous Hg^{2+} solutions, their fast capillary force driving diffusion into the hydrogel film brings Hg^{2+} and the grafted thiourea moiety together, which results in desulfurization of the thiourea groups and subsequent cyclization to produce the corresponding blue-light-emitting guanidine derivatives. b) Illustration of the fluorescent hydrogel-coated wearable sensing gloves that display visible "green-to-blue" emission color upon touching the Hg^{2+}-polluted food samples.
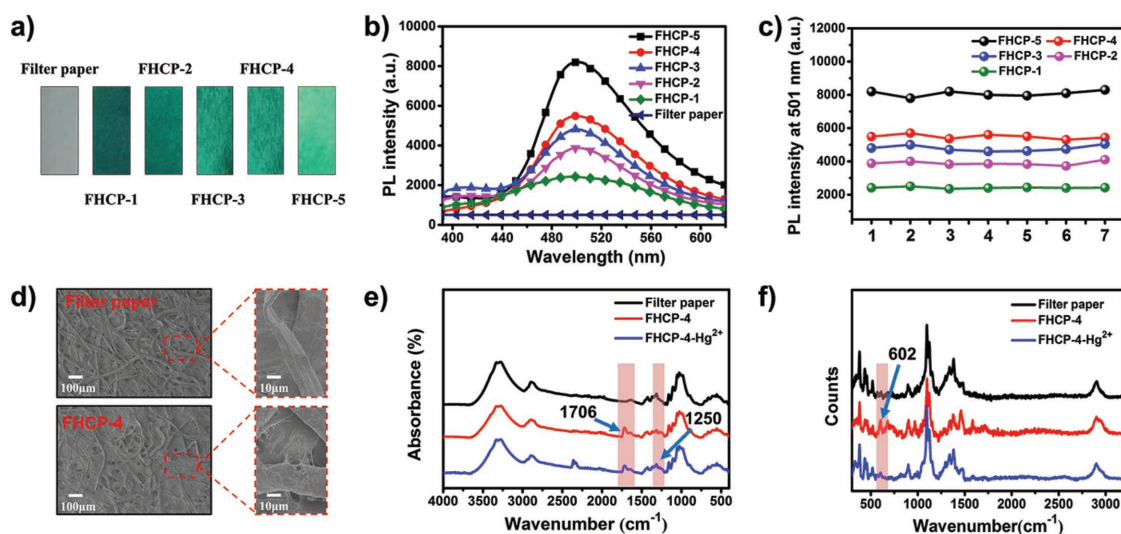

Figure 2. a) Photos of these FHCP sensors (FHCP-1–5) and the pristine filter paper taken under a handheld UV lamp at 365 nm; b) their fluorescence spectra; c) fluorescence intensities of these FHCP films at 501 nm measured from seven different spots of the films; d) SEM images of FHCP-4 film and pristine filter paper; e) ATR-FTIR and f) Raman spectra of the pristine filter paper and FHCP-4 film before and after exposure to Hg^{2+} solutions. Excitation at 365 nm for fluorescence spectra measurement.
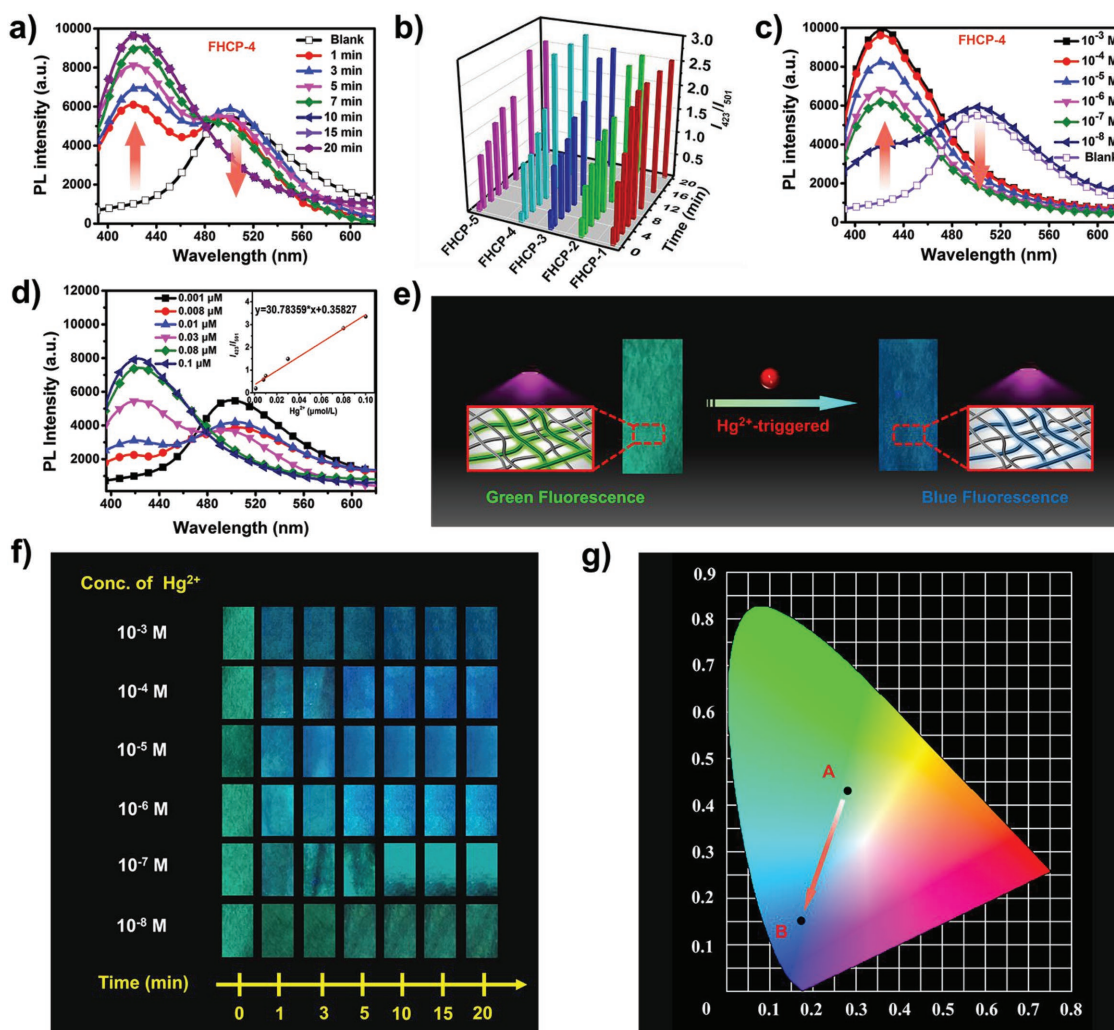
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Figure 3. a) Time-dependent fluorescence spectra of the FHCP-4 sensor immersed in aqueous Hg^{2+} solutions (10^{-3} M); b) time-dependent ratiometric fluorescence response (I_{423}/I_{501}, emission intensity ratio of "blue" (at 423 nm) and "green" (at 501 nm) band) of these FHCP-1–5 sensors; c,d) Hg^{2+}-concentration-dependent fluorescence spectra of the FHCP-4 sensor, d) inset shows I_{423}/I_{501} values of the FHCP-4 sensor as a function of Hg^{2+} concentration; e) schematic illustration of the visual Hg^{2+} detection mechanism; f) photos showing the time- and Hg^{2+}-concentration-dependent emission color change of the FHCP-4 sensor; g) the CIE chromaticity diagram before and after exposure to aqueous Hg^{2+} solutions. Excitation at 365 nm for fluorescence spectra measurement.

spectroscopy, and Raman spectra of pristine filter paper and hydrogel-coated filter paper. Moreover, the mechanical properties of our fluorescent hydrogel-coated paper film were also characterized (Figure S7, Supporting Information), which reveals that its maximum tensile strain becomes larger than the pristine filter paper. All of these results clearly show that fluorescent hydrogel has been successfully coated onto filter paper fiber to form multiple crosslinking networks.

2.2. Visual Hg^{2+} Detection Capacity

The Hg^{2+}-sensing capacity of these as-prepared hydrogel-coated fluorescent paper films was then investigated. As expected, a visible green-to-blue emission color change is noticed for all of these five paper films, as is evidenced by the fact that their fluorescence intensities around 423 nm significantly increase at the

expense of the gradual decrease of the emission band centered at 501 nm (**Figure 3**a and Figure S8, Supporting Information). This observation is due to the Hg^{2+}-induced transformation of thiourea units to imidazoline moieties (see ref.[19] and Figure 2e,f), resulting in a remarkable reduction in electron delocalization of the fluorogens. Importantly, this interesting Hg^{2+}-responsive intensity change of two different emission bands (at 501 and 423 nm, respectively) suggests that the developed paper films can work as a ratiometric probe. This finding is of interest because the ratiometric one can provide built-in correction of two emission bands for environmental effects and thus hold the potential to precisely quantify the Hg^{2+} concentration even in complex real-world aqueous samples. Figure 3b depicts the time-dependent ratiometric responses (intensity ratios of I_{423}/I_{501}) of these five hydrogel-coated paper films to aqueous Hg^{2+} samples of the same concentration. Note that the mercury ions induced desulfurization and cyclization reaction

can proceed quite fast at ambient conditions, which is in good agreement with the observation that the I_{423}/I_{501} values of all paper films rise immediately and nearly reach a peak value within 15 min (Figure 3b), indicating the fast response of our paper sensors.

To systematically investigate the Hg^{2+}-sensing capacity, the FHCP-4 film that displays the largest I_{423}/I_{501} values at given conditions (Figure 3b) was chosen as the typical example and subjected to systematical investigation. To record the Hg^{2+}-concentration-dependent fluorescence response, the hydrogel-coated paper film FHCP-4 was first immersed into aqueous Hg^{2+} solutions for 15 min at controlled conditions and its emission spectrum was then measured. As shown in Figure 3c,d and Figure S9 (Supporting Information), a new emission band centered at 423 nm appears and gradually rise with the increase of Hg^{2+} concentration, while the original emission band around 501 nm disappears. Remarkably, the developed paper film sensor is so sensitive that the extremely low-concentration Hg^{2+} (as low as 10^{-7} M) is sufficient to fully vanish its fluorescence peak at 501 nm (Figure 3c,d). Remarkably, its ratiometric linear detection range covers about nearly three orders of magnitude (ranging from 0.008 to 0.1×10^{-6} M) (Figure 3d inset) with a detection limit of 0.008×10^{-6} M, which was calculated according to the reported method. Its high sensitivity is further demonstrated by the visual detection experiments (Figure 3e,f), which reveals that a remarkable green-to-blue emission color change has been clearly observed after exposing the paper film to 10^{-7} M Hg^{2+} solutions within only several minutes. To visually display the naked-eye detection process, its CIE (Commission Internationale de L'Eclairage) coordinates are provided in Figure 3g. Similar Hg^{2+}-induced emission color change was also proved for FHCP-5 (Figure S10, Supporting Information).

Next, their emission response toward many other common metal ions was also studied to indicate the sensing selectivity of our paper film probes (**Figure 4**). As summarized in Figure 4a,b, no noticeable fluorescence change is observed for most of the studied metal ions, including K^+, Mg^{2+}, Al^{3+}, Ca^{2+}, Fe^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Fe^{3+}, Zn^{2+}, Pt^{2+}, and Na^+. High-concentration Ag^+ (10^{-3} M) is able to induce a slight blueshift of the emission band, which cannot yet be comparable to that of Hg^{2+}. Further evidence for the quite good sensing selectivity of our paper film probes comes from the visual detection experiments (Figure 4c) and anti-interference experiments (Figure 4d) conducted in aqueous mixture of Hg^{2+} and many other ions (including Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Pd^{2+}, Cu^{2+}, Cr^{3+}), indicating that the remarkable green-to-blue emission color change was only observed for Hg^{2+}.

To further prove the practical values of our flexible fluorescent hydrogel-coated paper film sensors, their photo- and storage-stability were then thoroughly investigated. As shown in Figure S11 (Supporting Information), the fluorescence emission spectra of the FHCP-4 film sample keep the same after being continuously irradiated under UV light for 100 min, suggesting their quite good photostability. To prove its storage-stability, the fresh-prepared FHCP-4 paper films were sealed under vacuum and stored at different conditions (e.g., tin foil or transparent package, see Figure S12a–f, Supporting Information) for several months. Figure S12g (Supporting Information)

summarizes the emission intensity ratio (F/F_0) of different storage time. The results clearly demonstrate that these F/F_0 values recorded at different storage conditions are still kept more than 96% after two month's storage, suggesting the excellent storage-stability of our paper film sensors. In order to further prove the probe's reliability after long-cycle operations, the Hg^{2+}-sensing performance of our hydrogel-coated paper film FHCP-4 has been studied after being bent 100 times. As shown in Figure S13 (Supporting Information), the results show that the FHCP-4 probe still exhibits satisfying ratiometric fluorescence response to Hg^{2+} even after being bent 100 times, demonstrating the reliability of the designed probe after long-cycle operations.

2.3. Detection of Hg^{2+} in Real-World Water/Food Samples

Enlightened by the satisfying Hg^{2+}-sensing performances of the developed flexible paper films, we then tried to test their possibility to determine the hazardous mercury ions in complex real-world water/food samples. For this purpose, two kinds of real-world water samples (tap water and river water from Yong River at Ningbo City) and four types of food samples (commercially available chicken, carp, potherb, and canna leaf purchased from the supermarket nearby) were selected as typical examples. In the experiments, these two real-world water samples were filtered before the measurement, while the food samples were processed into aqueous samples according to the standard method. As shown in **Figure 5**, all these measurements show a good agreement and demonstrate the negligible matrix effect of these real-world water/food samples, suggesting that the developed flexible hydrogel-coated paper film probes can be good candidates for real-world applications.

2.4. Adhesive-Assisted Wearable Hg^{2+} Detection

Considering the high toxicity of Hg^{2+} ions, it is better to assemble the as-prepared flexible paper sensors into integrated sensing appliances in order to protect the operators. To this end, a polydopamine(PDA)-mediated, one-pot surface coating approach was developed,[56] which enables the facile immobilization of Hg^{2+}-sensing paper sensors onto virtually any material surface (**Figure 6**a). In this study, the dopamine solutions codissolved with PVA (polyvinyl alcohol) polymer were coated onto surfaces of paper sensors during the polydopamine formation. This method is proved to be effective in immobilizing the Hg^{2+}-sensing paper films onto a wide variety of materials, including chemigum, polyethylene, orange peel, glass rod, leave, and steel (Figure 6b–f). More importantly, it is found that the Hg^{2+}-detection performance of our paper films is still maintained after surface modification. For example, visible Hg^{2+}-induced emission color change was also noticed when we put on the protecting gloves anchored with paper sensors to touch Hg^{2+}-polluted seafood (Figure 6g–i), suggesting the potential application of the designed sensing gloves for infield food analysis. This kind of integrated Hg^{2+}-sensing gloves may not only ensure safety of operators (especially for the untrained),
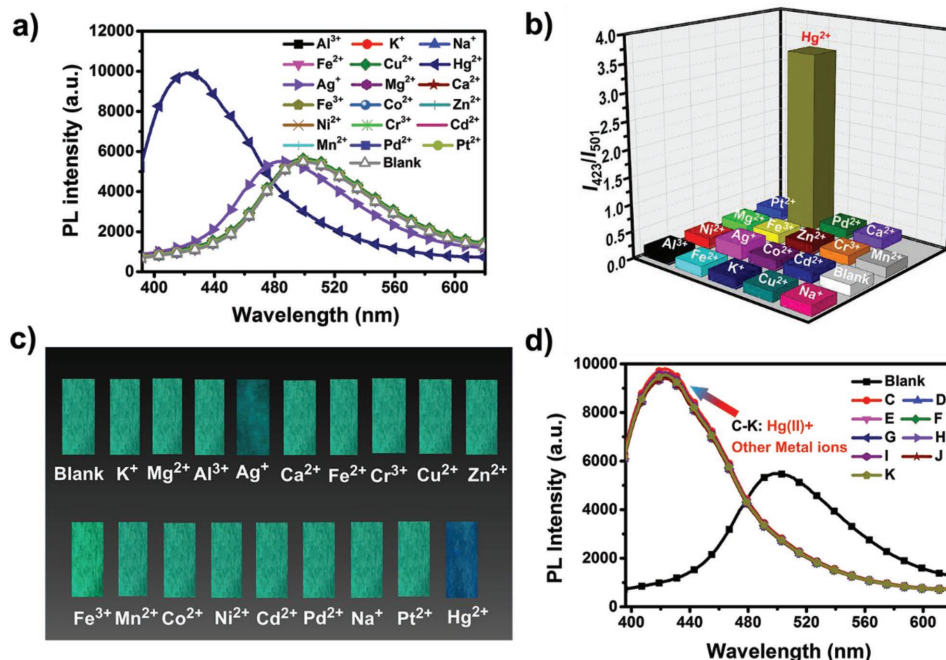
Figure 4. a) Fluorescence spectra of the FHCP-4 sensors toward many different metal ions; b) I_{423}/I_{501} values of the FHCP-4 sensor in response to many different metal ions; c) photos of the FHCP-4 sensor after being exposed to aqueous solutions of many different metal ions, which are taken under a handheld UV lamp at 365 nm; d) fluorescence spectra of the FHCP-4 sensors recorded in aqueous mixture of Hg^{2+} and many other ions. C–K: aqueous mixture of Hg^{2+} and other metal ion (Fe^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Zn^{2+}, Pd^{2+}, Cu^{2+}, Cr^{3+}). Excitation at 365 nm for fluorescence spectra measurement.

but also inspire the future development of more powerful integrated detection appliances for other food pollutants.

2.5. Wearable Sensing Gloves for Visible Hg^{2+} Detection

To further develop truly wearable sensing gloves suitable for in-field food and water detection, the fluorescent hydrogels were also directly coated onto glove fibers, where they can also exhibit visible emission color change in response to the toxic Hg^{2+} pollutant. As shown in **Figure 7**a, the hydrogel-coated gloves were prepared by in situ chemically crosslinking polymerization of Hg^{2+}-sensitive NDBCB, HEMA, and MBAA

cross-linker in tip part of the forefinger. The as-prepared gloves emit vivid green light under a handheld UV lamp and can be put on or taken off as easily as the untreated ones, demonstrating that wearable conformability of the gloves are not significantly affected by hydrogel postfunctionalization. Remarkability, the flexible hydrogel-coated gloves are proved to be quite durable and can withstand hundreds of bending and touching because of the good chemical, thermal, and mechanical stability of crosslinked sensing polymer hydrogels. This finding is of interest because food and water samples cannot be contaminated even if they are directly touched by this kind of wearable sensing gloves. More importantly, the hydrogel-coated gloves are capable of responding specifically
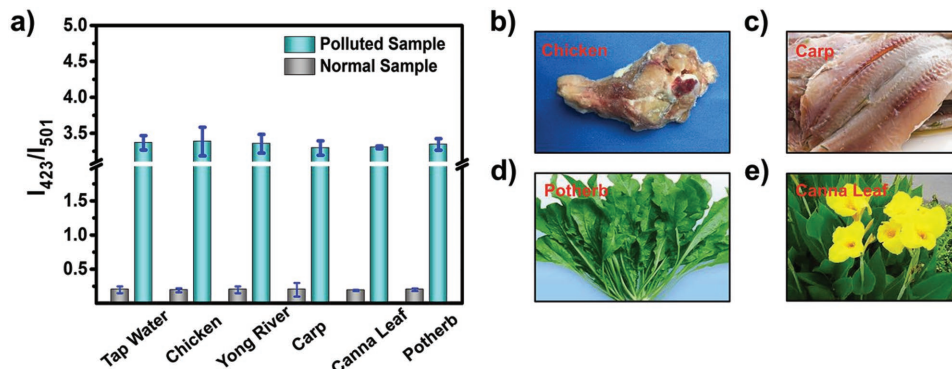

Figure 5. a) I_{423}/I_{501} values of the FHCP-4 sensor in response to some normal and Hg^{2+}-polluted real-world food/water samples; b) photos of many different food samples. In the experiments, two kinds of real-world water samples (tap water and river water from Yong River at Ningbo City) and four types of food samples (commercially available chicken, carp, potherb, and canna leaf purchased from the supermarket nearby) were selected as typical examples. Excitation at 365 nm for fluorescence spectra measurement.
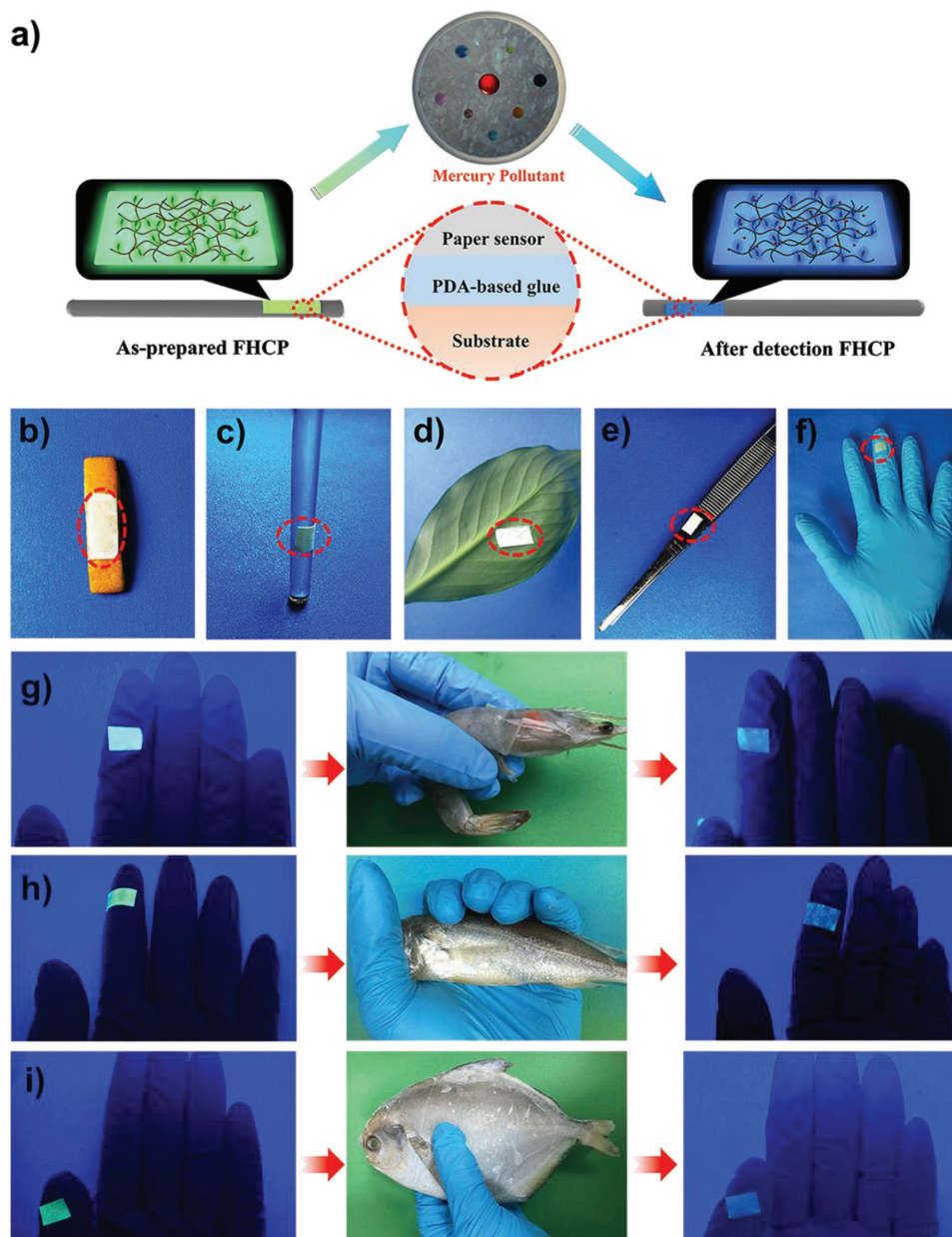
Figure 6. a) Schematic illustration of Hg^{2+}-sensing FHCP-4 film sensors that are immobilized onto a wide variety of materials via a polydopamine-mediated, one-pot surface coating approach, including b) orange peel, c) glass rod, d) leave, e) steel, and f) chemigum; g–i) visible Hg^{2+}-induced emission color change was noticed when we put on the protecting gloves anchored with paper sensors to touch Hg^{2+}-polluted seafood.

against the toxic Hg^{2+} ions, as is evidenced by the result that a remarkable green-to-blue emission color change was observed upon exposing the forefinger tip to Hg^{2+}-polluted sea shrimp (Figure 7b–d)). This is due to the Hg^{2+}-induced chemical reaction with NDBCB moieties to blueshift the fluorescence emission peaks (Figure 7e). In order to further prove its reliability after long-cycle operations, the Hg^{2+}-detection performance of the sensing gloves has been studied after being bent 100 times. As shown in Figure S14 (Supporting Information), the results show that the Hg^{2+}-induced fluorescence response of the developed sensing gloves is not affected even after being bent 100 times, demonstrating its good detection reliability

after long-cycle operations. It should be noted that this is the first flexible and wearable Hg^{2+} detection appliance, which is believed to represent a notable advance toward in-field food and water analysis. One can imagine that the Hg^{2+}-polluted meats, seafood, juice, and drinks will be easily discriminated if food processing packers get the opportunities to wear the developed new-concept sensing gloves. One can imagine that the Hg^{2+}-polluted river and tap waters will be timely detected if future housework gloves are functionalized by our sensing materials. In this way, this kind of wearable sensing gloves holds great possibility to protect us effectively against Hg^{2+}-polluted food and water samples.

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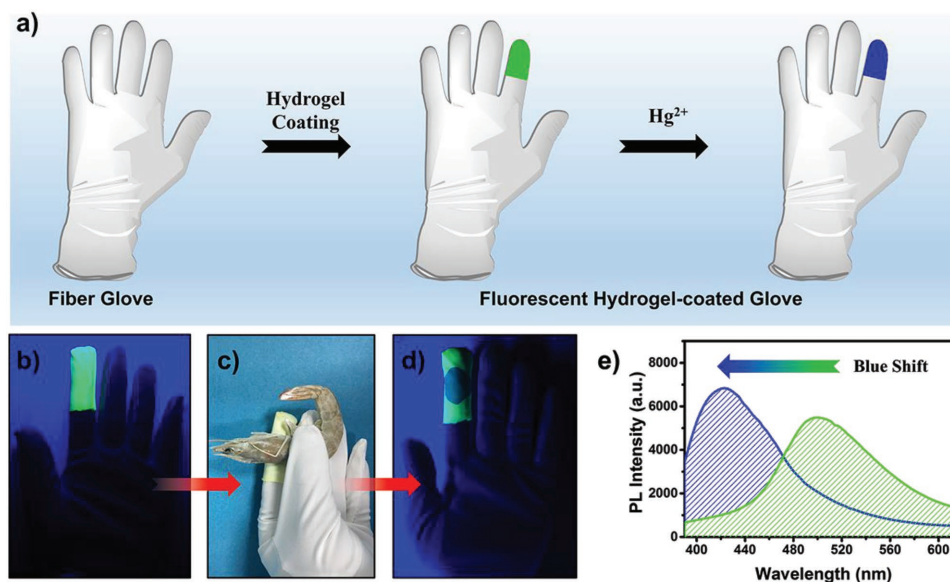MATERIALS
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Figure 7. a) Fabrication of the wearable fluorescent hydrogel-coated sensing gloves. the hydrogel-coated gloves were prepared by in situ chemically crosslinking polymerization of Hg^{2+}-sensitive NDBCB, HEMA, and MBAA cross-linker in tip part of the forefinger; b–d) photos showing emission color change of the hydrogel-coated wearable sensing gloves when exposing the forefinger tip to Hg^{2+}-polluted sea shrimp; e) fluorescence spectra of the wearable sensing gloves before and after being exposed to Hg^{2+}-polluted sea shrimp. Excitation at 365 nm for fluorescence spectra measurement.

3. Conclusion

We have presented a new kind of flexible paper/textile fiber-based film chemosensors for Hg^{2+} ions, which are prepared by in situ crosslinking the pristine filter paper/glove fiber with Hg^{2+}-sensitive fluorescent polymer hydrogel. The probe design relies on the specific chemical reaction between Hg^{2+} and the grafted thiourea moieties of film sensors to induce visible "green-to-blue" emission color change. Thanks to their hierarchical porous structures fixed by the interwoven paper/textile fibers, these flexible sensors allow much faster capillary force driven self-diffusion of aqueous Hg^{2+} solutions into the film matrix compared with the traditional rigid counterparts. Therefore, they are characterized with portability, high sensitivity, and enable facile Hg^{2+} detection even in complex real-world water and food systems. Furthermore, to facilitate infield detection and ensure safe operation, robust wearable Hg^{2+}-sensing gloves were then fabricated for the first time, which enables the visual and direct recognition of Hg^{2+}-polluted food and water samples by simply touching them. Considering the modular design principle of the flexible Hg^{2+}-sensing films and gloves, we are convinced that the reported strategy could inspire the future construction of more powerful wearable detection apparatus for other important food and water pollutants.

4. Experimental Section

Materials: HEMA (Aladdin Chemistry Co., Ltd.) was purified by column chromatography to remove the polymerization inhibitor. 2,2′-Azobis(2-methylpropionitrile) (AIBN, Aladdin Chemistry Co., Ltd.) was recrystallized from ethanol. 4-Bromo-1,8-naphthalic anhydride, allylamine hydrochloride, dopamine hydrochloride, and dimethyl sulfoxide were used as received from Energy Chemical

Co., Ltd. Anhydrous tetrahydrofuran (THF, 99.99%), $N,N′$-methylenebis(acrylamide), benzoyl isothiocyanate, and all testing nitrates of metal ions (Hg^{2+}, K^+, Mg^{2+}, Al^{3+}, Ag^+, Ca^{2+}, Fe^{2+}, Cr^{3+}, Cu^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}, Pd^{2+}, Fe^{3+}, Zn^{2+}, Pt^{2+}, and Na^+) were purchased from Sigma-Aldrich Co., Ltd. The DI water used in these experiments was obtained from a Milli-Q water purification system. Other solvents and reagents were used as received.

Characterization: ^{1}H-NMR spectra were measured on Bruker Advance AMX-400 Spectrometer in DMSO-d_6 using tetramethylsilane as the internal reference. Here, the chemical structures of ND-Br, ND-NH$_2$, and NDBCB were verified by ^{1}H-NMR spectroscopy. Raman spectra were collected on the R-3000HR Spectrometer (Raman Systems, Inc., R-3000 series) using a red LED laser (785 nm). FTIR spectroscopic measurements were conducted using a Micro FT-IR (Cary660+620) with resolution of 4 cm^{-1}. The morphology of freeze-dried paper film samples was measured by SEM equipped with energy-dispersive detector. Fluorescence spectra of hydrogel-coated paper film samples were recorded by Hitachi F-4600 Spectrofluorometer equipped with a 150 W Xenon (Xe) lamp at controlled conditions.

Immobilization of the Hg^{2+}-Sensing Paper Films onto Substrates of Interest by Polydopamine-Based Coating Approach: The coating solutions were first prepared by stirring 100 mg dopamine hydrochloride in 1 mL aqueous PVA solutions (10 wt%). After coating the mixed solutions onto surfaces of paper sensors during the polydopamine formation, the Hg^{2+}-sensing paper films can be firmly immobilized onto a wide variety of materials, including chemigum, polyethylene, orange peel, glass rod, leave, and steel.

Fabrication of FHCP/Textile Chemosensors: A typical synthetic procedure is described as follows: a mixed solution was first prepared by codissolving 2-hydroxyethyl methacrylate (306 mg; 285 µL), $N,N′$-methylenebis(acrylamide) (19.3 mg), AIBN (33.5 mg), and 1 mg NDBCB monomer in 5 mL DMSO. The FHCP/textile sensors were then fabricated by absorbing the mixed DMSO solutions onto paper or textile, and then in situ crosslinking polymerization at 65 °C for 8 h in a self-made glass mold. After being washed with ethanol, DMSO, and deionized water to fully remove the unreacted monomers, the hydrogel-coated paper film was dried at 60 °C to give FHCP-1. Other FHCP samples (see Table S1, Supporting Information) were prepared using similar synthetic procedures.

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Preparation of the Polluted Samples: The polluted samples were prepared by extracting the food sample (e.g., chicken, potherb, canna) with 70% HNO_3-10% H_2O_2 in order to fully remove the residual Hg^{2+} pollutant. More specifically, the food sample was first weighted and immersed into 70% HNO_3-10% H_2O_2 for 3 h. Transfer 4 mL of extracted solution to a 50 mL volumetric flask and dilute to volume. The extracted solutions were sealed in dark place at 4 °C before use.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

Conflict of Interest

The authors declare no conflict of interest.

Keywords

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