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# Ultrafast and Efficient Detection of Formaldehyde in Aqueous Solutions Using Chitosan-based Fluorescent Polymers

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**ABSTRACT:** Detection of toxic formaldehyde (HCHO) pollutant in aqueous solutions is of significant importance, because HCHO is widely found in aquatic food because of illicit addition or improper storage. Many small-molecule-based fluorescent probes, which relies on HCHO-specific formaldehyde-amine condensation or aza-Cope rearrangement reaction, have been developed in terms of facile operation and high selectivity. However, some primary challenging issues are the restricted sensitivity and long equilibrium response time caused by slow chemical reaction between these small-molecule-based sensors and low-concentration HCHO pollutant in testing samples. Herein, robust hydrophilic hydrazino-naphthalimide-functionalized chitosan (HN-Chitosan)-based polymeric probe is reported, which takes advantage of specific chemical reaction between HCHO and grafted hydrazino-naphthalimide groups to trigger "turn-on" fluorescence response. Superior to its small-molecule analogs, HN-Chitosan is based on random coil polymer chains of biopolymeric chitosan, which is thus capable of employing the cooperative binding effect of multiple hydrazino-naphthalimide recognition sites and adjacent hydroxyl groups to "enrich" low-concentration HCHO pollutant around the polymer chains via weak supramolecular interactions. Therefore, the HCHO-specific chemical reaction with grafted hydrazino-naphthalimide groups is significantly accelerated, resulting in the unprecedented ultrafast equilibrium fluorescence response (less than 1 min) and high sensitivity. Encouraged by its satisfying sensitivity, selectivity, fast response and wide linear detection range, we successfully expand its application to real-world food and water analysis. In view of the modular design principle of our polymeric probe, the proposed strategy could be generally applicable to construct powerful polymeric probes for ultrafast detection of other important pollutants.

As a notorious Category A1 carcinogen, formaldehyde is widely found in aquatic food because of illicit addition or improper storage. [1-3] Besides, it is also heavily consumed in chemical industry, resulting in some serious environmental water pollution accidents. [2] Therefore, facile detection of formaldehyde is of significant interest in order to protect people far from formaldehyde-polluted food and water samples. Nowadays, great efforts have been devoted to the development of formaldehyde sensing methods, including electrochemical, optical and biological sensors.[2,4] Among them, fluorescence-based approaches, having advantages in terms of facile operation and high sensitivity, are attracting increasing attention. Over the past decade, a large number of elegant formaldehyde-sensing fluorescent sensors have been reported, which take advantage of the specific formaldehyde-amine condensation[5-19] or aza-Cope rearrangement reaction[20-26] to realize highly selective detection. However, there still remains some difficult challenges. For example, most of these reported sensing materials are based on water-insoluble small molecules bearing hydrophobic conjugated organic fluorophores. Therefore, the sensing experiments have to be conducted in the volatile and toxic organic solvent or mixed aqueous solutions, thus significantly restricting their practical applications. Another primary challenging issue is the long equilibrium response time, which is believed to be caused by the relatively slow chemical reaction between the developed sensing molecules and low-concentration HCHO pollutant at ambient conditions.

Polymeric probes are promising candidates to overcome the limitations of these conventional small molecule-based ones. [27-33] Specially designed polymeric sensing materials are typically constructed by incorporating many functional binding sites in the side chains or on the backbones. Therefore, polymeric probes could take advantage of the cooperative effects of multiple recognition sites to bind the low-concentration analyte more efficiently, resulting in desirable signal amplification and fast fluorescence response.[34-40] Additionally, it is also quite easy to incorporate hydrophobic sensing moieties into the water-soluble functional polymers by simple post-modification or copolymerization strategies, thus avoiding the use of toxic and volatile organic solvent in detection experiments.[34-35] However, although numerous robust polymeric sensing materials have been successfully constructed for a large number of environmental or food pollutants,[27, 41-42] little efforts have been done to develop water-soluble and fast-response polymeric probes for formaldehyde.

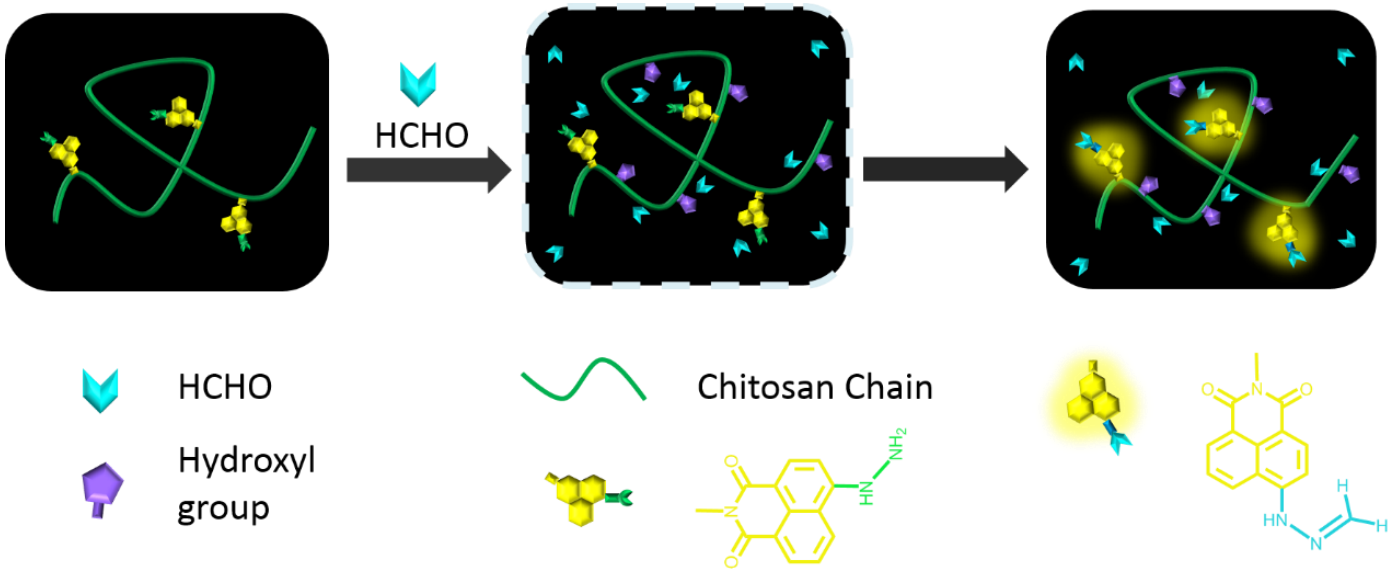


**Figure 1.** HCHO-sensing mechanism of the developed HN-Chitosan polymer probe. The probe design depends on the specific chemical reaction between HCHO and hydrazino group to trigger "turn-on" fluorescence response of naphthalimide fluorophores. HN-Chitosan is based on hydrophilic random coil polymer chains of biopolymeric chitosan grafted with a large density of hydroxyl groups and hydrazino-naphthalimide recognition sites. Therefore, it is capable of taking advantage of the cooperative effect of multiple recognition sites and adjacent hydroxyl groups to "enrich" low-concentration HCHO pollutant around the random coil polymer chains via weak supramolecular interactions, resulting in ultrafast fluorescence response and high sensitivity.

In this work, we presented a robust hydrophilic polymeric probe, the hydrazino-naphthalimide-functionalized chitosan (HN-Chitosan) polymer, which enables ultrafast, selective and sensitive detection of low-ppm-level HCHO pollutant in pure water solutions. The probe design depends on the specific chemical reaction between HCHO and hydrazino group to trigger "turn-on" fluorescence response of naphthalimide fluorophores (Figure 1).[7] However, unlike previously reported small-molecule-based analogs, which involve only HCHO-triggered chemical reaction at the molecular level, HN-Chitosan is based on hydrophilic random coil polymer chains of biopolymeric chitosan grafted with a large density of hydroxyl groups and hydrazino-naphthalimide recognition sites (**Figure 1**). Therefore, our polymeric probe is capable of taking advantage of the cooperative effect of multiple recognition sites and adjacent hydroxyl groups to "enrich" low-concentration HCHO pollutant around the random coil polymer chains via weak supramolecular interactions, thus significantly accelerating the chemical reaction between HCHO and hydrazino-naphthalimide groups. As a result, ultrafast fluorescence response (less than 1 min) and high sensitivity are obtained, which represent a notable advance in the field of HCHO detection because almost all the previously reported reaction-based probes suffer from long equilibrium response time (20~30 min). Moreover, HN-Chitosan is also characterized with wide linear detection range and pretty good photo-stability, which encouraged us to further expand its application into real-world food and water analysis.

## EXPERIMENTAL SECTION

**Chemicals and Reagents.** 4-Bromo-1,8-naphthalic anhydride (98%) was obtained from Energy Chemical Co. Chitosan (50-100 mpa.s, 0.5% Acetic acid at 20 ºC) was purchased from Tokyo Chemical Industry Co., LTD. DMSO (99%), methanol (99.5%). hydrazine hydrate (85%), ethanol (99.7%), N-acetyl-glycine (98%), sodium pyruvate (99%), chloral (99.5%), acetaldehyde (40%), calcium chloride (96%) and sodium chloride (99.5%) were purchased from Shanghai Sinopharm Chemical Reagent Co. L-cysteine (99%), L-arginine (99%), N-acetyl-cysteine (99%), Magnesium sulfate (99.5%) and Ferric chloride hexahydrate (99%) were obtained from Sigma-Aldrich Company.

**Instruments and Measurements.** $^1$H-NMR spectra were conducted using Bruker Advance AMX-400 Spectrometer in DCl, $CF_3COOD$ or DMSO-$d_6$. ATR-FT-IR spectra were recorded on Micro FT-IR (Cary 660+620). Fluorescence and UV-Vis spectra were measured by Hitachi F-4600 Spectrofluorometer (excitation at 440 nm for all fluorescence measure-ments) and PerkinElmer Lambda 950 UV−vis−NIR spectrometer in a 10 mm path length cell, respectively.

**Synthesis of HN-Chitosan.** NBr-Chitosan was first synthesized according to the reported method.[43] Briefly, under $N_2$ protection, 3.6 g chitosan and 0.4 g 4-bromo-1,8-naphthalic anhydride were added into a 250 mL round-bottom flask containing 200 mL DMSO. After being stirred at 80 ºC for 3 hours, the reaction mixture was filtered immediately and washed with hot DMSO to totally remove the unreacted 4-bromonaphthalic anhydride. After being subsequently washed by water and methanol, NBr-Chitosan was obtained as a brown colored solid.

To obtain HN-Chitosan, the freshly prepared NBr-Chitosan polymer (1.0 g) was mixed with 20 mL ethanol into a round-bottom flask, 3. 8 mL hydrazine hydrate was then added to the mixture. After being stirred at 80 ºC for 4 h, the mixture was cooled to room temperature and filtered to give a colored solid. HN-Chitosan was finally obtained after being washed with ethanol. Other HN-Chitosan samples with different hydrazino-naphthalimide contents could be facilely prepared by varying the feed ratios.

**HCHO detection in real-world food and water samples.** These food samples were bought from nearby supermarket.

Their extracted aqueous samples were prepared by soaking 2.0 grams of chicken, 1.32 grams of salmon, and 1.68 grams of pork in deionized water containing 0.1 M hydrochloric acid, respectively. Water samples (0.1 M hydrochloric acid) were prepared using tap water of Ningbo city, instead of deionized water. The concentrated solutions of HN-Chitosan-3 was prepared by dissolving 83 mg polymer in 250 mL deionized water containing 0.1 M hydrochloric acid. In the measurement experiments, 1 mL HN-Chitosan-3 solution was first mixed with 1 mL pristine extracted food or water samples at controlled conditions (25 $^{o}$C). Then the fluorescence intensities of the mixed solutions were measured. Experiments to measure the HCHO concentration in HCHO-polluted food and water samples were conducted using a similar method.

## RESULTS AND DISCUSSION

**Synthesis of the HN-Chitosan polymer and the model compound NAHN.** As shown in **Figure 2a**, the hydrazino-naphthalimide-functionalized chitosan (HN-Chitosan) polymer was synthesized by a two-step chemical reaction starting from the commercially available bio-based chitosan. Briefly, 4-bromo-1,8-naphthalic anhydride is mixed with the chitosan suspension in DMSO at elevated temperature to produce 4-bromo-naphthalimide-functionalized chitosan, which then reacts with excess hydrazine hydrate in ethanol to give the targeted HN-Chitosan polymer. On the basis of the possible modulation of the fluorescent features and formaldehyde-sensing ability via changes in the content of hydrazino-naphthalimide moieties, four HN-Chitosan samples were prepared by varying the feed ratio. **Table S1** and **Table S2** summarize the preparation formula of these four polymer samples. All of these four HN-Chitosan samples are colored solid and their color gradually darkens with an increase of the hydrazino-naphthalimide content (**Figure 2b**). HN-Chitosan-1~3 are readily soluble in hydrochloric acid solutions, while HN-Chitosan-4 bearing the highest naphthalimide content is only slightly soluble. We have tried to characterize the HN-Chitosan polymer by $^{1}$H NMR (**Figure S1** and **S2**) and IR spectra (**Figure S3**). However, the signal peaks of naphthalimide moieties are not evident because of their quite low grafted density. Dialysis experiments were then conducted, in which these purified HN-Chitosan polymers are first dissolved in acid solutions and dialysed in dialysis bags with molecular weight cut-off of 3500 Da for several days. It is found that these polymer solutions still keeps highly colored, suggesting that naphthalimide fluorogens have been covalently grafted to chitosan polymer. **Figure S4** depicts the normalized UV-Vis spec-tra of HN-Chitosan-1~3 polymers, in which a broad absorbance band ascribed to naphthalimide group was observed around 400 nm, indicating successful functionalization of naphthalimide fluorogens to chitosan polymer.[44] According to the UV-Vis absorbance using the reported method (**Figure S5** and **S6**),[45] the bromonaphthalimide content of BrN-Chitosan-3 and the hydrazino-naphthalimide content of HN-Chitosan-3 were calculated to be 1.76 wt% and 1.10 wt%, respectively. Therefore, the grafting rate of the bromo groups by hydrazine groups in HN-Chitosan-3 is calculated to be 64.7%.

As a model compound, N-allyl-4-hydrazino-naphthalimide (NAHN) was synthesized according to a similar two-step reaction route (**Figure 2c**). Briefly, 4-bromo-1,8-naphthalic anhy-

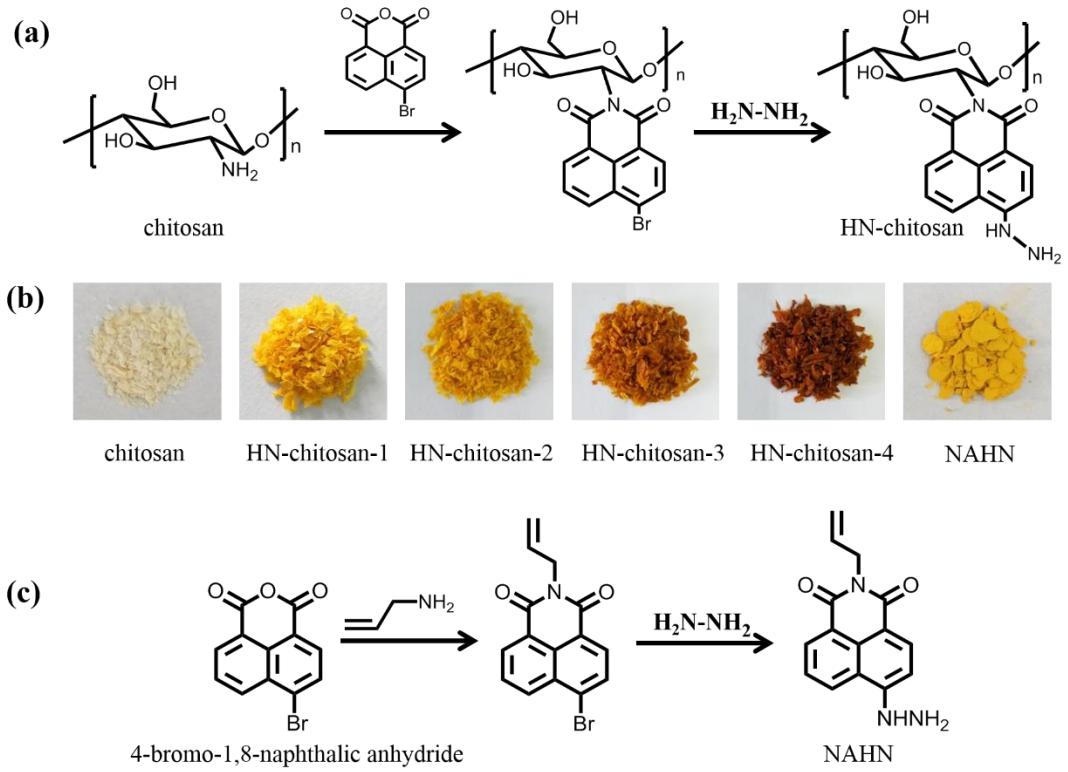


**Figure 2.** Synthetic procedures of the hydrazino-naphthalimide-functionalized chitosan (HN-Chitosan) polymers (a) and the small-molecule model compound NAHN (c) as well as their photos taken under room light (b).

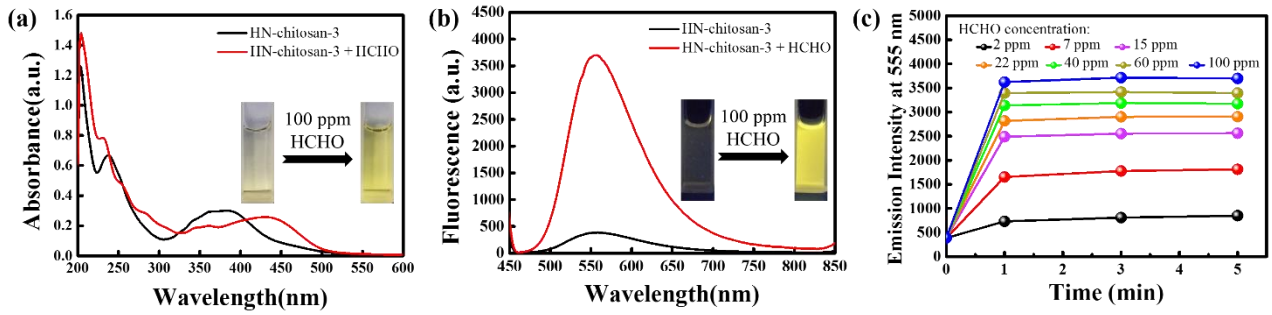


**Figure 3.** (a) UV-Vis and (b) fluorescence spectra of aqueous HN-Chitosan-3 solutions (0.166 mg/mL) in the absence and presence of 100 ppm HCHO. Inset images show their photos taken under room light and UV light at 365 nm, respectively. (c) Time-dependent fluorescence intensity change of aqueous HN-Chitosan-3 solutions at 555 nm in the presence of HCHO ranging from 2~100 ppm.

dride is heated in ethanol solution of allyl amine to produce N-allyl-4-bromo-naphthalimide, which is then treated with excess hydrazine hydrate to give the model compound NAHN. As a known compound, its chemical structure is characterized by $^1$H NMR spectrum (**Figure S7**), which exhibits typical signal peaks of naphthalimide (around 7~8 ppm) and allyl (4~6 ppm) groups.

**HCHO-Sensing Studies.** To screen the polymer probe with satisfying sensing property, the fluorescence response of these HN-Chitosan polymers to HCHO was first studied. As shown in **Figure S8**, the aqueous solutions of HN-Chitosan-1~3 at the same concentration of naphthalimide moieties are nearly non-fluorescent under a hand-held UV lamp at 365 nm. This is because there exists adjacent hydrazino groups to naphthalimide moieties, which can act as strong fluorescence quenchers to the naphthalimide fluorogens via a known PET (photoinduced electron transfer) process.[7,32] However, upon addition of trace amount HCHO, "turn-on" fluorescence response is immediately observed for all samples (**Figure S8**), because the above-mentioned PET process from hydrazine receptor to naphthalimide fluorophores will be significantly suppressed by the fast chemical reaction between HCHO and hydrazine groups. As summarized in **Figure S8**, HN-Chitosan-3 solution immediately exhibits intense emission enhancement and becomes highly yellow-light-emitting in the presence of 100 ppm HCHO, accompanying with noticeable UV-Vis absorbance and color change under room light (**Figure 3a**). Nevertheless, aqueous solutions of HN-Chitosan-1 and HN-Chitosan-2 only emit weak yellow light at given conditions. Therefore, the HN-Chitosan-3 probe with the most remarkable fluorescence response was selected as the typical example and subjected to systematical studies in this work.

Since the HCHO detection of the polymeric probe is reaction-based, it is necessary to study the kinetic profiles in the presence of HCHO. Therefore, the time-dependent fluorescence response of HN-Chitosan-3 to HCHO were investigated. Typically, the experiments were conducted in covered cuvettes at controlled conditions. Fluorescence spectra of the aqueous HN-Chitosan-3 solutions were recorded at different time intervals after the addition of HCHO. As expected, a remarkable fluorescence intensity enhancement was immediately observed after the addition of ppm-level HCHO (**Figure 3b**). To our surprise, its signal response is proved to be very fast. As shown in **Figure 3c**, the emission intensity of HN-Chitosan-3 probe quickly rises and nearly levels off within only 1 min for aqueous HCHO solutions of various concentrations (from 2 ppm to 100 ppm). It should be noted that the developed HCHO-sensing HN-Chitosan-3 polymer probe is of significant interest and represents a small but notable advance, because it usually takes about 30 min for most of its small-molecule analogs (**Figure 4**) (such as the model compound NAHN and many other previously reported probes[2]) to reach equilibrium fluorescence response. The underlying reason for this uniquely ultrafast spectroscopic response is believed to lie in the special chemical structure of the HN-Chitosan-3 polymer probe, where a number of recognition sites (hydrazino groups) and adjacent hydroxyl groups are

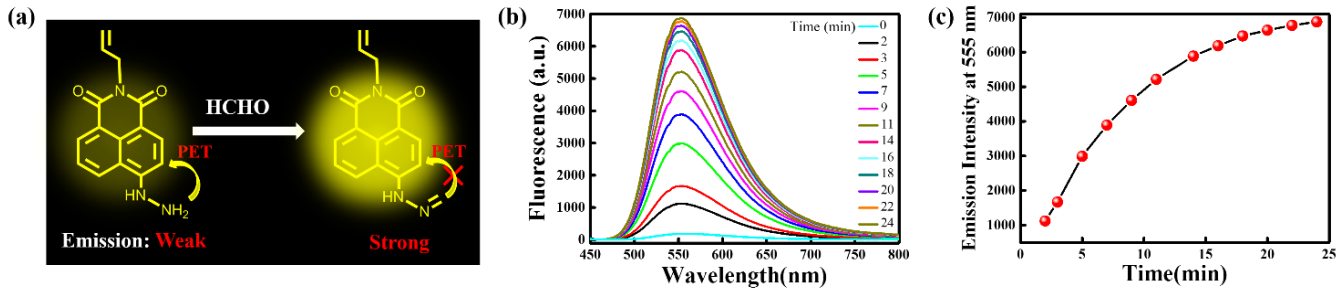


**Figure 4.** (a) Illustration of the HCHO-sensing mechanism of the model compound NAHN. (b) Time-dependent fluorescence spectra of NAHN solutions in the presence of 20 ppm HCHO. (c) Time-dependent fluorescence intensity change of NAHN solutions at 555 nm in the presence of 20 ppm HCHO.

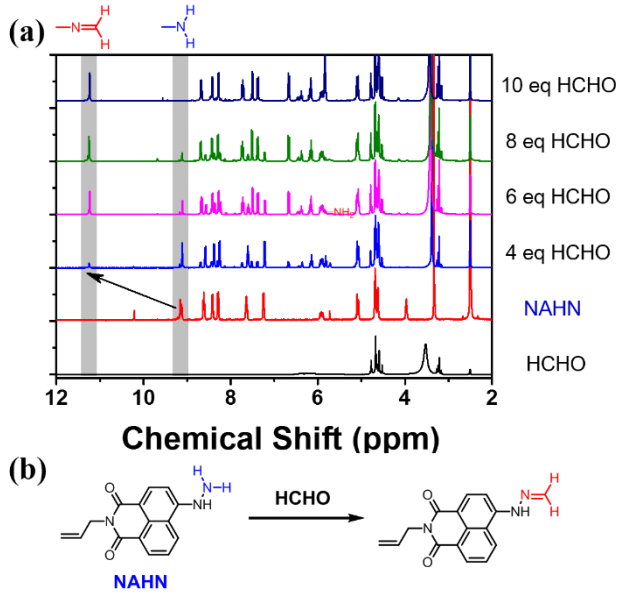


**Figure 5.** (a) $^1$H-NMR titration spectra of the model compound NAHN with increasing amount of HCHO; (b) the chemical reaction between HCHO and the NAHN compound.

grafted along the polymer chain. It is thus the cooperative effect of these grafted multiple recognition sites that results in significantly enhanced binding efficiency of the HN-Chitosan-3 polymer towards HCHO. As a consequence, equilibrium spectroscopic response time of our polymer probe is significantly shortened comparing with their small-molecule analogs.

To further verify the HCHO-sensing mechanism of the developed polymeric probes, $^1$H-NMR titration experiments were conducted. Considering the low resolution of polymeric spectra, the small-molecule-based NAHN probe was used as a model compound to record the $^1$H-NMR titration spectra. As can be seen in **Figure 5**, upon stepwise addition of HCHO, the -$NH_2$ signal around 9.1 ppm gradually decreases and eventually disappears. Meanwhile, a new signal ascribed to the –N=$CH_2$ group appears and significantly increase. Further evidence comes from the $^{13}$C NMR measurement, which shows a typical signal peak of –N=$CH_2$ around 163.1 ppm (**Figure S9**). These results, together with the above-mentioned fluorescence titration experiments, clearly demonstrate that it is the chemical reaction of HCHO and -$NH_2$ group that cause the remarkable "turn-on" fluorescence response.

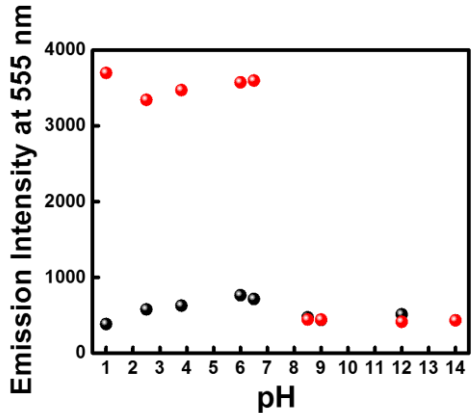


**Figure 6.** Fluorescence intensity changes (at 555 nm) of the polymeric probe HN-Chitosan-3 (0.166 mg/mL) in aqueous solutions at different pH values in the absence (black dot) or presence (red dot) of 100 ppm HCHO for 3 min.

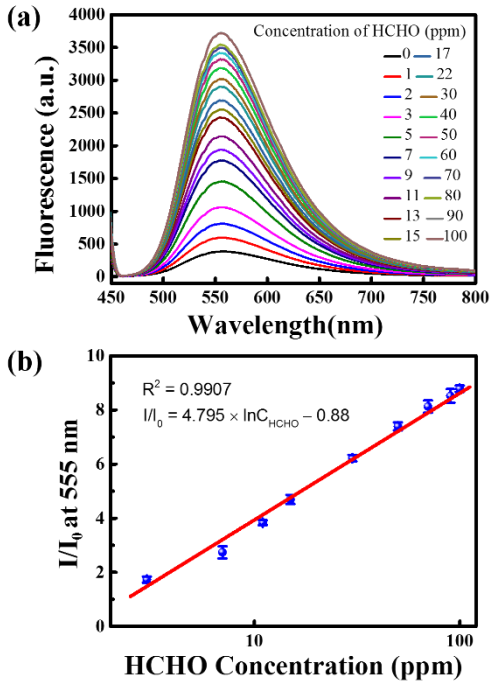


**Figure 7.** (a) HCHO-concentration-dependent fluorescence spectra of aqueous HN-Chitosan-3 solutions (0.166 mg/mL), which were recorded 3 minutes after HCHO addition. (b) Fluorescence intensity ratio (I/Io) of aqueous HN-Chitosan-3 solutions (0.166 mg/mL) at 555 nm versus the concentration of HCHO in the range from 1–100 ppm. I/Io is defined as the ratio of the emission intensity of HN-Chitosan-3 solution in the presence of HCHO to that of its pristine solution.

Next, pH-dependent kinetic studies were conducted in order to screen the ideal conditions for HCHO detection. As summarized in **Figure 6**, the study shows that the fluorescence response of our polymeric probe is more favorable in acid conditions to basic conditions. Remarkably, HN-Chitosan-3 is proved to exhibit remarkable HCHO-triggered fluorescence enhancement over a wide pH range (from pH=1 to pH=6.5, see **Figure 3b** and **S10**), suggesting the developed polymeric probe holds great potential to work well at various testing conditions. It should be noted that the HCHO-triggered fluorescence response of HN-Chitosan-3 probe is more remarkable in acid conditions than basic conditions. This is because that acid can serves as catalysts to significantly accelerate the chemical reaction between the grafted hydrazino-naphthalimide groups and HCHO.[7] Based on these results, HCHO-concentration-dependent fluorescence spectral changes of the HN-Chitosan-3 polymer probe were thus conducted at 0.1 M HCl (pH=1) solutions, because 0.1 M HCl solutions are usually used to extract the HCHO pollutant from real-world food samples. Herein, the HCHO-concentration-dependent emission spectra of aqueous HN-Chitosan-3 solutions were then recorded 3 min after formaldehyde addition. As summarized in **Figure 7**, the emission intensities of aqueous HN-Chitosan-3 solution steadily increase with higher HCHO concentration. The fluorescence response is

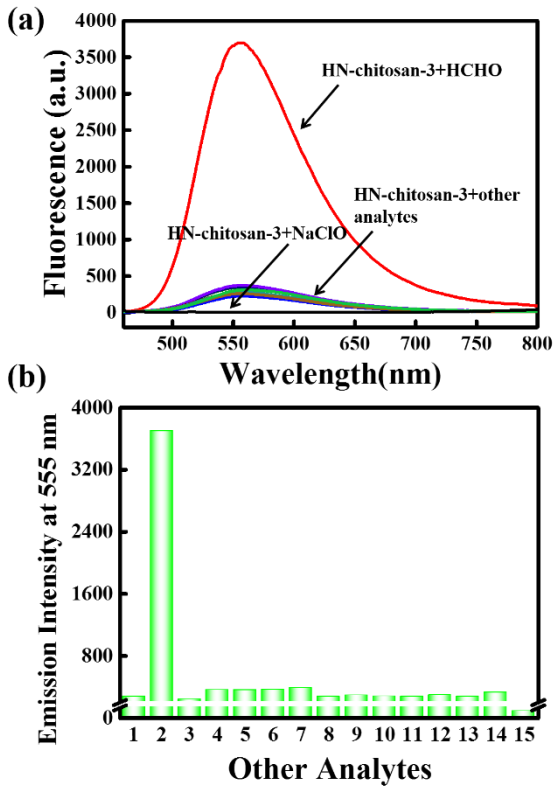


**Figure 8.** (a) Fluorescence spectra of aqueous HN-Chitosan-3 solutions (0.166 mg/mL) in the presence of HCHO or other possibly coexisting analytes as well as (b) their emission intensities at 555 nm (1) blank; (2) FA; (3) $Fe^{3+}$; (4) $Ca^{2+}$; (5) $NO_3^-$; (6) $Mg^{2+}$; (7) $Cl^-$; (8) L-cysteine; (9) L-arginine; (10) N-acetylcysteine; (11) N-acetylglycine; (12) sodium pyruvate; (13) chloral; (14) acetaldehyde; (15) NaClO.

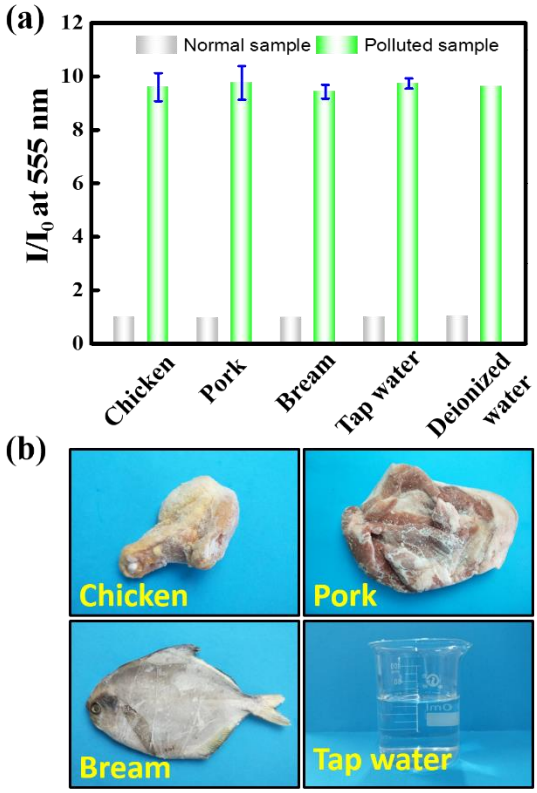


**Figure 9.** (a) Fluorescence intensity ratio (I/Io) of HN-Chitosan-3 solutions (0.166 mg/mL) at 555 nm for extracted aqueous solutions of three commercially available food samples (chicken, bream and pork purchased from the supermarket nearby) and tap water of Ningbo city. The HCHO concentration in all the extracted solutions of these complex samples is 100 ppm. (b) Photos of these real-world food and water samples.

so remarkable that nearly 10-fold emission intensity enhancement is observed in the presence of only 100 ppm HCHO. The developed polymeric sensor is also proved to be very sensitive, as is evidenced by the fact that obvious emission intensity change could be clearly observed in the presence of only 1 ppm HCHO. Remarkably, its logarithmic linear detection range covers nearly three orders of magnitude (ranging from 1~100 ppm), thus holding great potential to quantify the formaldehyde concentration in various aqueous samples. The observed logarithmic response is primarily attributed to the specially designed chemical structure of the developed polymeric HN-Chitosan-3 probe, where many sensing moieties (hydrazino groups) are located along the polymer chain. In the presence of low-concentration HCHO, the fast chemical reaction between HCHO and the grafted sensing moieties will lead to fast response enhancement. However, with the proceeding of the reaction, the grafted sensing moieties are gradually consumed and its concentration decreases accordingly. Therefore, the chemical reaction speed gradually decreases even if the HCHO concentration increases. As a result, the fluorescence intensity of HN-Chitosan-3 rises rapidly and gradually reaches a plateau with increasing HCHO concentration (**Figure S11**), thus leading to a logarithmic linear relationship between fluorescence intensity ratio of our probe and HCHO concentration. According to According to the widely-accepted method,[46] the theoretical detection limit of our sensor was calculated to be about 0.05 ppm (1.66 uM) using the following equation, which can be comparable with many reported fluorescent probes (**Table S3**).

Detection Limit=3σ/slope=3*0.07969/4.795=0.05 ppm (1.66 uM); σ=0.07969 (1)

Furthermore, the sensing selectivity and photo-stability of HN-Chitosan-3 polymer probe were studied. As summarized in **Figure 8**, the results suggest that no significant fluorescence enhancement was observed for tens of potentially coexisting interfering compounds, including some common aldehyde compounds and many other possibly coexisting chemical species in real-world food and water samples (e.g. $Fe^{3+}$, $Ca^{2+}$, $NO_3^-$, $Mg^{2+}$, $Cl^-$, L-cysteine, L-arginine, N-acetyl-cysteine, N-acetylglycine, sodium pyruvate, chloral and acetaldehyde). These investigations clearly demonstrate the quite good selectivity of our polymer probe. Further studies show that the emission intensities of aqueous HN-Chitosan-3 solutions keep nearly constant under given measurement conditions (placed in air or after irradiation at 440 nm for 25 min), indicating the pretty good photostability of the developed polymer probe in air or under irradiation (**Figure S12** and **S13**). More remarkably, it is found that the HCHO concentrations determined by HN-Chitosan-3 polymer probe, despite being a bit higher (**Figure S14**), could still be comparable with those obtained by the well-known pararosaniline colorimetric method[47] within experimental error, suggesting great potential applications of our polymeric probes.

**Detection of HCHO in real-world water and food samples.** Encouraged by the satisfying HCHO-sensing sensitivity, selectivity, wide linear detection range and photo-stability of the developed HN-Chitosan-3 polymer probe, we try to test its possibility to measure the concentration of this pollutant in the complex real-world water and food samples. Herein, we selected tap water of Ningbo city and extracted aqueous solutions of three commercially available food samples (chicken, bream and pork purchased from the supermarket nearby) as typical examples. As can be seen from **Figure 9**, quite good consistency was obtained, demonstrating that the matrix effect of these water and food samples is negligible. These results are quite encouraging, suggesting the potentially wide and practical application of the developed polymeric sensor.

## CONCLUSIONS

We have presented a hydrophilic hydrazino-naphthalimide-functionalized chitosan polymer (HN-Chitosan) for HCHO detection, which is based on the HCHO-induced specific chemical reaction to trigger "turn-on" fluorescence response of naphthalimide fluorophores. By taking advantage of the cooperative binding effect of the grated multiple recognition sites and adjacent hydroxyl groups, HN-Chitosan is proved to be highly sensitive to ppm-level HCHO pollutant in aqueous solutions with ultrafast equilibrium response time (less than 1 min). This represents a notable advance in the field of HCHO detection because it usually takes 20~30 minutes for its small-molecule analogs to reach emission equilibrium. Moreover, HN-Chitosan is characterized with wide linear detection range (1~100 ppm) and pretty good photo-stability. Especially, it is capable of quantifying the HCHO concentration is many real-world food and water samples, suggesting its huge potential practical application. Furthermore, in view of the modular design principle of HN-Chitosan, the proposed strategy could be generally applicable to construct powerful polymeric chemosensors for ultrafast detection of other important pollutants in the future.

## ASSOCIATED CONTENT

**Supporting Information**.
The Supporting Information is available free of charge on the ACS Publications website at DOI:

Synthetic formula, $^1$H NMR and absorption spectra of the polymeric probes and the model compound, as well as many selected spectra and data refered in the paper.

This material is available free of charge via the Internet at http://pubs.acs.org.

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### Author Contributions

P.L., W.L., W.Q.W. and T.C. conceived and designed the experiments. P.L., D.Z. performed the experiments. Y.C.Z. contributed to materials. P.L., W.L., D.Z., Y.C.Z., W.Q.W. and T.C. co-wrote the paper.

### Notes

The authors declare no competing financial interest.

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## ABBREVIATIONS

HN-Chitosan, hydrazino-naphthalimide-functionalized chitosan; NBr-Chitosan, 4-bromo-1,8-naphthalic anhydride-functionalized chitosan; NAHN, N-allyl-4-hydrazino-naphthalimide.

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# TOC Figure (For ToC only)