A Novel Turn-On Fluorescent Sensor Based on Sulfur Quantum Dots and MnO₂ Nanosheet Architectures for Detection of Hydrazine

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Abstract: In this paper, the SQDs@MnO₂ NS as the probe was applied to construct a novel “turn-on” fluorescent sensor for sensitive and selective detection of hydrazine (N₂H₄). Sulfur quantum dots (SQDs) and MnO₂ nanosheets (MnO₂ NS) were simply mixed, through the process of adsorption to prepare the architectures of SQDs@MnO₂ NS. The fluorescent emissions of SQDs@MnO₂ NS play a key role to indicate the state of the sensor. According to the inner filter effect (IFE) mechanism, the state of the sensor at the “off” position, or low emission, under the presence of MnO₂ NS, is which the ultraviolet and visible spectrum overlaps with the fluorescence emission spectrum of SQDs. Under the optimal conditions, the emission was gradually recovered with the addition of the N₂H₄, since the N₂H₄ as a strong reductant could make the MnO₂ NS converted into Mn²⁺, the state of the sensor at the “on”. Meanwhile, the fluorescent sensor possesses good selectivity and high sensitivity, and the detection concentration of N₂H₄ with a wide range from 0.1 µM to 10 mM with a detection limit of 0.072 µM. Furthermore, actual samples were successful in detecting certain implications, indicating that the fluorescent sensor possesses the potential application ability to monitor the N₂H₄ in the water.

Keywords: sulfur quantum dots; MnO₂ nanosheet; hydrazine; fluorescence probe

1. Introduction

Hydrazine (N₂H₄) has attracted particular attention due to its strong reducibility and weak alkalinity in applications such as pesticides, pharmaceuticals, fuels, organic dyes, and so on [1,2]. Meanwhile, the toxicity and harm of N₂H₄ could not be neglected due to its water-solubility. It could damage the lungs, eyes, skin, and some system diseases when exposed to the N₂H₄ surroundings for an extended period of time [3,4]. Hence, the development of a facile and sensitive measure for N₂H₄ is considerable. In the past decades, many analytical methods have been reported, including chromatography, electrochemical, fluorescent, titrimetric, colorimetry, and mass spectrometry [5–7]. The fluorescent method is a powerful technique to detect N₂H₄, due to a comprehensive consideration of the factors including the low cost, simple operation, and rapid analysis.

The fluorescent method consists of constructing a fluorescent probe to observe the fluorescence intensity enhancement, or quenching, for the qualitative and quantitative analysis present of the targets. The fluorescent probe materials are commonly applied in the fluorescent sensor field similar to quantum dots (QDs) [8–10], organics [11,12], metal-organic framework [13–15], and metal nanoclusters [16,17]. Therein, the sulfur quantum dots (SQDs) is a novel and attention the QDs, which retain the advantage of the traditional optical performance of QDs while overcoming potential issues of the toxicity of the heavy metal QDs. Thus, it is widely applied in the fluorescent probes, biological sensors, and cell
imaging fields [18–20]. Lei et al., take the one-pot to prepare the polyvinyl alcohol-capped SQDs as the fluorescent probe for detection of Fe$^{3+}$ and temperature in cells [21].

Nowadays, the various probes of fluorescent are being investigated and developed to detect N$_2$H$_4$. Based on the aggregation caused quenching effect [22–24], aggregation-induced emission effect [25–27], the excited-state intramolecular proton-transfer effect [28–30], and photo-induced electron transfer [31,32], probes such as 5-(9-phenyl-9H-carbazol-3-yl)thiophene-2-carbaldehyde [22], salicylaldehyde Schiff’s base [25], p-TNS [28], and 5-chlorothiophene-2-carbonyl chloride [31]. Using these mechanisms to detect N$_2$H$_4$ method is relatively mature, with little room for growth. Therefore, we introduced the inner filter effect (IFE) mechanism to rapidly detect N$_2$H$_4$, which is the absorption of the excitation and/or emission light by the quencher (MnO$_2$) leading to the intensity decrease [33].

Herein, we first introduced the IFE mechanism to establish a “turn-on” fluorescent sensor for the detection of N$_2$H$_4$. The sensing strategy is illustrated in Figure 1; SQDs combined with MnO$_2$ nanosheet (MnO$_2$ NS) to prepare SQDs@MnO$_2$ NS architectures. The SQDs alone have a strong fluorescence intensity and the MnO$_2$ NS has nearly no fluorescence under the same experimental conditions. The SQDs@MnO$_2$ NS possesses a lower intensity compared to the SQDs, due to the MnO$_2$ NS as a full-of-all adsorbed material in the ultraviolet and visible (UV-Vis) spectrum, which could overlap with the fluorescence emission spectrum of SQDs, led to the fluorescence intensity quenching. Meanwhile, at this stage, the state of the fluorescent sensor is off. However, the emission of fluorescent is recovered under the N$_2$H$_4$ present condition, with the addition concentrations the state is gradually turned on. Benefits of the sensor for quantitatively detecting N$_2$H$_4$ was successfully constructed by monitoring the fluorescent intensity of SQDs@MnO$_2$ NS. Furthermore, this approach possesses the potential for a practical application, due to its ability to effectively identify the N$_2$H$_4$ in the real samples of water.

![Figure 1. Mechanism of “turn-on” fluorescence sensor based on SQDs@MnO$_2$ NS for detecting N$_2$H$_4$.](image)

2. Materials and Methods

2.1. Materials

Sublimed sulfur, polyethylene glycol (PEG-400), Tetramethylammonium hydroxide (TMA-OH), and NaOH were provided by Shanghai Aladdin Biochemical Technology Co. (Shanghai, China). MnCl$_2$·4H$_2$O, K$_2$S$_2$O$_8$ were acquired from Sinopharm Chemical Reagent Co., Ltd. (Tianjin, China). N$_2$H$_4$ (v/v 80%) was purchased from Sigma Chemical Co., Ltd. (Shanghai, China). The prepared solutions of all experiments used ultrapure water (18.2 MΩ cm) from a water purification system.
2.2. Apparatus

Transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HR-TEM) measurements was carried out using a JEOL-2010F (200 kV) (JEOL, Tokyo, Japan). The ultraviolet and visible (UV-Vis) absorption spectra were examined with a UV-Vis spectrophotometer (TU-1901, Beijing, China). Fourier-transform infrared (FT-IR) spectroscopy was performed using a Nicolet 5700 Fourier transform infrared spectrometer (Shimadzu, Tokyo, Japan). The prepared nanomaterials were characterized by X-ray diffraction (XRD, LabX XRD-6000 (Shimadzu, Tokyo, Japan)). Elemental analysis was recorded by X-ray photoelectron spectroscopy (XPS, Thermo Scientific Escalab 250Xi, USA). Fluorescence spectra were collected using an F-4700 fluorescence spectrophotometer (HITACHI, Tokyo, Japan).

2.3. Synthesis of SQDs and MnO₂ NS

SQDs were synthesized according to a literature method [34]. Briefly, the sublimed sulfur powder (1.4 g) was added to a mixed solution of PEG-400 (3 mL) and NaOH (50 mL, 0.08 g mL⁻¹) stirring at 70 °C for 24 h. During the period, the color of the solution changed gradually from dark-yellow to light-yellow, and then added H₂O₂ (3 mL) to each, the obtained solution was termed as SQDs. The prepared SQDs were introduced in the dialysis membrane with the molecular weight of 1000 Da to remove unreacted molecular dialysis for 72 h each 12 h to change the water. Then, the light-yellow solid was acquired by freeze-drying at −20 °C for 24 h, and the SQDs were stored at 4 °C for further use.

MnO₂ NS were prepared with reference to previous literature [35]. Firstly, TMA·OH (12 mL, 1.0 M) solution was introduced in MnCl₂·4H₂O (10 mL, 0.3 M) at the 50 mL round-bottomed flask. Afterward, the H₂O₂ (2 mL, 30%) solution was slowly added to the mixed solution vigorously stirring at room temperature for 24 h. The acquired dark brown solution was centrifuged and rinsed with ultra-water and CH₃OH several times. Last, the obtained product of MnO₂ NS was dried at room temperature.

2.4. The SQDs@MnO₂ NS Fluorescent Probe Detection N₂H₄

The mixture solution of SQDs@MnO₂ was obtained by SQDs and MnO₂ NS mixed to stand for 1 h at room temperature. Next, the different concentrations of N₂H₄ solution (0.1 μM–10 mM) were added to the SQDs@MnO₂ (1 mL) to react for 10 min at room temperature and perform fluorescence spectroscopy tests. Finally, a standard curve line was constructed between various concentrations of N₂H₄ and the recovery value of fluorescence intensity. In addition, the fluorescence probe selectivity, stability, and repeatability were studied under the optimal conditions.

2.5. Detection of Actual Samples

The fluorescence probe of SQDs@MnO₂ NS was selected specifically for N₂H₄. To verify the performance in the actual sample of the probe, this was applied to detect the environmental water samples. Actual samples were acquired from the lake and river in Yantai. Briefly, the water samples were filtered with the 0.45 μm filter membrane to remove impurities. Then, to detect the N₂H₄ in the lake and river were used to prepare various concentrations of N₂H₄ (0.1 μM, 10 μM, and 10 mM) reaction for 10 min to test fluorescence spectroscopy, respectively. Three experiments were performed in parallel, and RSD was calculated.

3. Results

3.1. Characteristics of SQDs, MnO₂ NS, SQDs@MnO₂

The morphology of SQDs, MnO₂ NS, and SQDs@MnO₂ architectures was characterized by HR-TEM and TEM. As shown in Figure 2a,b, the morphology of SQDs was spherical particles with good distribution, and the size of SQDs was calculated mainly to be 3.5 ± 0.5 nm. Next, the morphology of MnO₂ NS was investigated presenting a large two-dimensional ultrathin planar structure (inset of Figure 2c). Meanwhile, the struc-
3. Results  
3.1. Characteristics of SQDs, MnO$_2$ NS, and SQDs@MnO$_2$ NS  

As can be seen in Figure S1c, the XPS survey spectrum of SQDs was recorded, which demonstrated that the prepared SQDs on the surface have an amount of sulfite group by adsorbing since the huge amount of S. The peaks located at 641.8 eV belonged to MnO$_2$, and the characteristic peaks of Mn 2p appeared at 644.3 eV, 649.1 eV, which was identified with the previously reported work [36]. As can be seen in Figure S1c, the XPS survey spectrum of SQDs@MnO$_2$ NS was composed of four elements of C, O, N, and Mn. In the spectrogram of the Mn 2p element in Figure S1b, the band energy peaks located at 641.8 eV belonged to MnO$_2$, and the characteristic peaks of Mn 2p appeared at 644.3 eV, 649.1 eV, which was identified with the previously reported work [36]. Additionally, the XPS survey spectrum of SQDs@MnO$_2$ NS was successfully prepared.

Figure 2. (a) HR-TEM images of SQDs; (b) the diameter distribution of the SQDs; (c) TEM images of MnO$_2$ NS with HR-TEM images of MnO$_2$ NS (inset); (d) TEM images of SQDs@MnO$_2$ NS with HR-TEM images of SQDs@MnO$_2$ NS (inset).

To further study the elements of SQDs and MnO$_2$ NS, X-ray photoelectron spectroscopy (XPS) was analyzed. In Figure S1a, the MnO$_2$ NS was composed of four elements of C, O, N, and Mn. In the spectrogram of the Mn 2p element in Figure S1b, the band energy peaks located at 641.8 eV belonged to MnO$_2$, and the characteristic peaks of Mn 2p appeared at 644.3 eV, 649.1 eV, which was identified with the previously reported work [36]. As can be seen in Figure S1c, the XPS survey spectrum of SQDs was recorded, which peaks corresponding to the elements of C, O, and S, respectively. The spectrum of the S 2p region in Figure S1d exhibits two peaks at 162.3 eV and 163.2 eV, which were due to the elemental S. The band peaks at 166.5 eV, 168.2 eV, and 169.3 eV were respective corresponding to the SO$_3^{2−}$ (2p$_{2/3}$), SO$_3^{2−}$ (2p$_{2/3}$) or SO$_2^{2−}$ (2p$_{1/2}$), and SO$_3^{2−}$ (2p$_{1/2}$), which demonstrated that the prepared SQDs the surface has an amount of sulfite group by adsorbing since the huge surface and small volume [34]. Additionally, the XPS survey spectrum of SQDs@MnO$_2$ was shown in Figure 3a, in which elements of S 2p (Figure 3b) and Mn 2p (Figure 3c) correspond to the SQDs and MnO$_2$, indicating the SQDs@MnO$_2$ was successfully prepared.
To further verify the SQDs, MnO$_2$ NS, and SQDs@MnO$_2$ NS were successful in preparation, the UV-Vis spectra were shown in Figure 4. The broad absorption bands of MnO$_2$ NS the range from 280 to 650 nm a weak peak around 360 nm, which is due to the d-d transition of Mn$^{4+}$ ions [37]. The UV-Vis absorption spectra of SQDs and SQDs@MnO$_2$ both have peaks at 313 nm and 350 nm, which might be ascribed to the S$^{2-}$ and S$_8^{2-}$ adsorbed on the surface of SQDs [34]. However, the values of peaks of SQDs@MnO$_2$ were lower than SQDs due to the adsorption of SQDs on MnO$_2$ NS. The excitation (Ex) and emission (Em) spectra of fluorescence of SQDs@MnO$_2$ were shown in Figure 4b, the Em wavelength at 484.2 nm under the excitation wavelength of 380 nm, which is like the previous work [38].

3.2. Optimization of Experimental Parameters

We have investigated the experimental parameters to acquire the optimal conditions, including the excitation wavelength for SQDs, the concentration of MnO$_2$ NS, the volume ratio of N$_2$H$_4$ to MnO$_2$ NS, and the pH of the SQDs and SQDs@MnO$_2$ NS solution. As illustrated in Figure 5a, the synthesized of SQDs detected under the different excitation wavelengths at 330–420 nm, the intensity of fluorescent behaved a general trend of rising first and then falling, and the maximum emission at 400 nm. Thus, the excitation wavelength of SQDs at 400 nm was chose as the optimal wavelength. As shown in Figure 5b, with the increase of the concentration of MnO$_2$ NS, the quenching emission values of SQDs were increased, and the fluorescent intensity of SQDs was nearly all the quenched at the concentration of MnO$_2$ NS at 10 mg mL$^{-1}$. Hence, 10 mg mL$^{-1}$ was selected as the optimum concentration of MnO$_2$ NS for the next use. In addition, the quenching behavior of SQDs@MnO$_2$ about different concentrations of MnO$_2$ NS for better visualization in Figure S2, which obviously noted that the MnO$_2$ NS possesses a huge surface that could package the SQDs. The volume ratio of N$_2$H$_4$ to MnO$_2$ NS was shown in Figure 5c, the
N$_2$H$_4$ volume-specific gravity increased the emission was gradually recovered, and the volume ratio reached 2:1 of N$_2$H$_4$ to MnO$_2$ NS the emission intensity reached the maximum recovery values. Furthermore, the SQDs increased with pH from 5 to 12, which had no influence on its emission, while introducing the MnO$_2$ NS the emission of SQDs values significantly decreased (Figure 5d). However, with the increased pH, the quench of emission degree was decreased. On this basis, we selected the pH = 7 as the experiment condition, considering the pH of the environment water. As shown in Figure 5e, the fluorescence of SQDs intensity was decreasing when the MnO$_2$ was added. The molar ratio of SQDs@MnO$_2$ was increased to 10:4 the fluorescence intensity reached its lowest. After, the molar ratio of SQDs@MnO$_2$ over 10:4 the fluorescence intensity was a tiny increase. Thus, the molar ratio of 10:4 has been chosen for the further experiment. In addition, the response time of SQDs@MnO$_2$ with N$_2$H$_4$ was recorded in Figure 5f, when 10 min of reaction was the Δ$I = 30$ (Δ$I = $ intensity (2 min)-intensity (1 min)), and the value of Δ$I$ was nearly stable. Therefore, the SQDs@MnO$_2$ with N$_2$H$_4$ 10 min of reaction as the optimal react time.

Figure 5. Optimization of conditions: (a) optimal excitation wavelength for SQDs; (b) concentrations of MnO$_2$ NS; (c) volume ratio of N$_2$H$_4$ to MnO$_2$ NS; (d) Different pH; (e) the molar ratio of SQDs@MnO$_2$ (a–h (SQDs: MnO$_2$ = 10:0, 10:1, 10:2, 10:3, 10:4, 10:5, 10:6, 10:7)); (f) the response time of SQDs@MnO$_2$ with N$_2$H$_4$.

3.3. Fluorescence Spectra Analysis of N$_2$H$_4$ Sensing

The MnO$_2$ NS nearly a total absorption in UV-Vi’s spectrum at the 280 nm to 650 nm in this study, which could effectively quench the fluorescence of SQDs due to the IFE mechanism. However, with the N$_2$H$_4$ was introduced once the emission was recovered, demonstrating that the MnO$_2$ NS was reduced to Mn$^{2+}$ in the presence of N$_2$H$_4$. Beneficial from this result, a simply “turn-on” sensor was constructed.

Under the optimum experiment condition, the analytical performance of the fluorescent sensor was investigated to detect N$_2$H$_4$ with various concentrations. As exhibited in Figure 6a, the fluorescence intensity was increased with the N$_2$H$_4$ concentration gradually added, indicating that the more reduction matter the more Mn$^{2+}$ in the detected solution. The recovery values of fluorescence intensity of the logarithm of N$_2$H$_4$ concentration in the range from 0.1 µM to 10 mM, with a limit of detection (LOD) were calculated to be 0.072 µM according to the 3σ/s. Figure 6b demonstrates that the linear equation was
I = 1010.4 logc(N₂H₄) + 8116.2 with a correlation coefficient of 0.9972, where I was the recovery intensity value of fluorescence. The comparison of the proposed methods to detect N₂H₄ with previous reports was listed in Table 1. It was significantly observed that the SQDs@MnO₂ NS probe possessed the lower LOD and satisfactory linear range over other approaches.

Figure 6. (a) The response of SQDs@MnO₂ NS fluorescent probe to N₂H₄ solution with different concentrations (0.1 μM–10 mM); (b) The linear relationship between fluorescence intensity and N₂H₄ concentrations.

Table 1. Comparison of several different methods for N₂H₄ detection.

| Method          | Linear Range (M) | Detection Limit (M) | Ref.     |
|-----------------|------------------|---------------------|----------|
| ZY8 a           | 1.6 × 10⁻⁷–6.2 × 10⁻⁵ | 1.6 × 10⁻⁷          | [39]     |
| PBAS b          | 0–2 × 10⁻⁵       | 4.1 × 10⁻⁷          | [25]     |
| CEFN c          | 0–6 × 10⁻⁵       | 9.6 × 10⁻⁸          | [40]     |
| HBTM d          | 0–1.4 × 10⁻⁴     | 2.9 × 10⁻⁷          | [30]     |
| SQDs@MnO₂ NS    | 10⁻⁵–10⁻²        | 7.2 × 10⁻⁸          | This work|

a 3-hydroxyflavone; b Salicylaldehyde Schiff’s bases; c nopinone; d 5-acetyl-2-hydroxybenzaldehyde and 2-aminothiophenol.

3.4. Selectivity, Stability, and Repeatability

To evaluate the specificity of the probe of SQDs@MnO₂ NS, the selective as one of the most important factors was investigated under similar reaction conditions. The various ions including Ni²⁺, Co²⁺, K⁺, Ca²⁺, Fe²⁺, Na⁺, Cd²⁺, Cu²⁺, Cr³⁺, SO₄²⁻, NO₃⁻, Cl⁻, OH⁻, CO₃²⁻ were used as interference agents, these ions are the common positive ions and anions present in the environment. As shown in Figure 7a, the fluorescence intensity was negligible present the interference agents compared to have N₂H₄, indicating that the preparation probe has a strong anti-interference ability and accuracy detect N₂H₄ in environment water.

Figure 7. (a) The effect of different cations and anions on the fluorescence intensity of SQDs@MnO₂ NS fluorescent probe; (b) the fluorescence intensity stability of SQDs in two weeks; (c) the reproducibility of SQDs in 5 groups.
In addition, to further assess the stability of the SQDs@MnO$_2$ NS fluorescent probe, the good stability of SQDs was an important means to verify. As depicted in Figure 7b, the fluorescence intensity of SQDs was continuous detection for 14 days under similar experimental conditions, it was noticed that the intensity have a slow decrease and the degree was insignificant. Interestingly enough, after a month of observing the intensity of SQDs was only a tiny different compared with them before a month, illustrating that the SQDs@MnO$_2$ NS possessed a high stable fluorescence performance. For reproducibility, as can be seen from Figure 7c, the test was performed under the five sets of parallel solutions of SQDs in the same environment, all of the measured fluorescence intensities possess the semblable value with an outstanding RSD of 1.1%. This result was successful in confirming that the SQDs have preeminent reproducibility. Meanwhile, they have the potential benefit to the synthesis and application of the SQDs@MnO$_2$ NS. These results demonstrated that the proposed sensor has good selectivity, stability, and repeatability for the analysis of N$_2$H$_4$.

3.5. Detection of N$_2$H$_4$ in Real Water Samples

To investigate the practicability of the probe of SQDs@MnO$_2$ NS, it was applied to detect N$_2$H$_4$ in real samples. Three parallel water samples were obtained from the local lake and river for conducting the standard recovery test. The results were shown in Table 2, the N$_2$H$_4$ was detected in the lake, river, serum, and saliva, where the recovery ranged from 90.21% to 109.1%, and the RSD was 0.9% to 4.5%, demonstrating that the fluorescent probe possesses practicability with promise for future applications.

Table 2. Recoveries for detecting N$_2$H$_4$ in real samples ($n = 3$).

| Sample   | Added (M) | Found (M) | Recovery (%) | RSD (%) |
|----------|-----------|-----------|--------------|---------|
| Lake water | 10$^{-2}$ | 1.073 $\times$ 10$^{-2}$ | 107.3 | 1.4 |
|          | 10$^{-5}$ | 0.9021 $\times$ 10$^{-5}$ | 90.21 | 2.1 |
|          | 10$^{-7}$ | 0.9624 $\times$ 10$^{-7}$ | 96.24 | 1.1 |
| River water | 10$^{-2}$ | 1.091 $\times$ 10$^{-2}$ | 109.1 | 2.2 |
|          | 10$^{-5}$ | 1.032 $\times$ 10$^{-5}$ | 103.2 | 0.9 |
|          | 10$^{-7}$ | 0.9254 $\times$ 10$^{-7}$ | 92.54 | 1.7 |
| Serum    | 10$^{-2}$ | 0.9691 $\times$ 10$^{-2}$ | 96.91 | 4.5 |
|          | 10$^{-5}$ | 0.9967 $\times$ 10$^{-5}$ | 99.67 | 1.9 |
|          | 10$^{-7}$ | 1.027 $\times$ 10$^{-7}$ | 102.7 | 2.8 |
| Saliva   | 10$^{-2}$ | 0.9851 $\times$ 10$^{-2}$ | 98.51 | 3.1 |
|          | 10$^{-5}$ | 0.9741 $\times$ 10$^{-5}$ | 97.41 | 1.6 |
|          | 10$^{-7}$ | 1.016 $\times$ 10$^{-7}$ | 101.6 | 2.9 |

4. Conclusions

In summary, we have developed a “turn-on” fluorescent sensor based on the SQDs@MnO$_2$ NS architectures for the detection of N$_2$H$_4$. The MnO$_2$ NS has a broad absorption band of MnO$_2$ NS at 280 to 650 nm, which could effectively quench the emission of fluorescence of SQDs, owing to the IFE mechanism. However, the fluorescent emission was recovered presenting the N$_2$H$_4$ analysis target with a concentration in the range of 0.1 µM to 10 mM, with a LOD of 0.072 µM. In addition, the fluorescent sensor was successfully applied in real samples indicating the SQDs@MnO$_2$ NS probe was possess the potential ability to detect the N$_2$H$_4$ in the environmental water samples.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/nano12132207/s1, Figure S1: (a) XPS survey spectrum of MnO$_2$ NS and SQDs; Figure S2: The quenching behavior of SQDs@MnO$_2$ about the concentrations of MnO$_2$ NS.
Author Contributions: Conceptualization: X.L. and X.W.; methodology: X.L. and X.W.; software: X.L., W.G., F.L., C.T., and X.Z.; validation: X.L., X.W., F.L., C.T., and X.Z.; formal analysis: X.L. and X.W.; investigation: C.T., L.Z., W.G., and X.Z.; resources: C.T., L.Z., and X.Z.; writing—original draft preparation: X.L. and X.Z.; writing—review and editing: F.L., C.T., and X.Z. All authors have read and agreed to the published version of the manuscript.

Funding: This research was financially supported by the National Natural Science Foundation of China (21778047), and the Natural Science Foundation of Shandong Province (grant no. ZR2021MB024).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Conflicts of Interest: There are no conflict to declare.

References

1. Khushboo; Umar, A.; Kansal, S.K.; Mehta, S.K. Highly-sensitive and selective detection of hydrazine at gold electrode modified with PEG-coated CdS nanoparticles. Sens. Actuators B Chem. 2013, 188, 372–377. [CrossRef]

2. Chen, S.; Hou, P.; Wang, J.; Liu, L.; Zhang, Q. A highly selective fluorescent probe based on coumarin for the imaging of N₂H₄ in living cells. Spectrochim. Acta Part A Mol. Biomol. Spectrosc. 2017, 173, 170–174. [CrossRef] [PubMed]

3. Mazzolou-Ardakani, M.; Khoshroo, A.; Hosseinzadeh, L. Simultaneous determination of hydrazine and hydroxylamine based on fullerene-functionalized carbon nanotubes/ionic liquid nanocomposite. Sens. Actuators B Chem. 2015, 214, 132–137. [CrossRef]

4. He, Y.P.; Zheng, J.B.; Dong, S.Y. Ultrasonic-electrodeposition of hierarchical flower-like cobalt on petalage-like graphene hybrid microstructures for hydrazine sensing. Analyst 2012, 137, 4814–4818. [CrossRef] [PubMed]

5. Haghhighi, B.; Hamidi, H.; Bozorgzadeh, S. Sensitive and selective determination of hydrazine using glassy carbon electrode modified with Pd nanoparticles decorated multivalved carbon nanotubes. Anal. Bioanal. Chem. 2010, 398, 1411–1416. [CrossRef]

6. He, Y.P.; Zheng, J.B.; Sheng, Q.L. Cobalt nanoparticles as sacrificial templates for the electrodeposition of palladium nanomaterials in an ionic liquid, and its application to electrochemical sensing of hydrazine. Microchim. Acta 2012, 177, 479–484. [CrossRef]

7. Koçak, S.; Aslı¸sen, B. Hydrazine oxidation at gold nanoparticles and poly (bromocresol purple) carbon nanotube modified glassy carbon electrode. Sens. Actuators B Chem. 2014, 196, 610–618. [CrossRef]

8. Do Nascimento, A.S.; Cabral, P.E.; Fontes, A.; Santos, B.S.; de Carvalho, F.R.; Stragevitch, L.; Leite, E.S. CdSe quantum dots as fluorescent nanomarkers for diesel oil. Fuel 2019, 239, 1055–1060. [CrossRef]

9. Liu, M.P.; Liu, T.; Xiao, D. A FRET chemsensor based on graphene quantum dots for detecting and intracellular imaging of Hg²⁺. Talanta 2015, 143, 442–449. [CrossRef]

10. Bogomolova, A.; Aldissi, M. Real-time aptamer quantum dot fluorescent flow sensor. Biosens. Bioelectron. 2011, 26, 4099–4103. [CrossRef]

11. Li, X.C.; Zhao, Y.P.; Yin, J.L.; Lin, W.Y. Organic fluorescent probes for detecting mitochondrial membrane potential. Coord. Chem. Rev. 2020, 420, 213419. [CrossRef]

12. Zhao, X.J.; Huang, C.Z. Small organic molecules as fluorescent probes for nucleotides and their derivatives. Trend. Anal. Chem. 2010, 29, 354–367. [CrossRef]

13. Wang, Q.Y.; Ke, W.Q.; Lou, H.Y.; Han, Y.H.; Wan, J.M. A novel fluorescent metal-organic framework based on porphyrin and AIE for ultra-high sensitivity and selectivity detection of Pb²⁺ ions in aqueous solution. Dyes Pigment. 2021, 196, 109802. [CrossRef]

14. He, R.; Wang, Y.L.; Ma, H.F.; Yin, S.G.; Liu, Q.Y. Eu³⁺-functionalized metal-organic framework composite as ratiometric fluorescent sensor for highly selective detecting urinary 1-hydroxyxpyrene. Dyes Pigment. 2018, 151, 342–347. [CrossRef]

15. Zhou, Z.D.; Wang, C.Y.; Zhu, G.S.; Du, B.; Yu, B.Y.; Wang, C.C. Water-stable europium(III) and terbium(III)-metal organic frameworks as fluorescent sensors to detect ions, antibiotics and pesticides in aqueous solutions. J. Mol. Struct. 2022, 1251, 132009. [CrossRef]

16. Halawwa, M.I.; Lai, J.; Xu, G. Gold nanoclusters: Synthetic strategies and recent advances in fluorescent sensing. Mater. Today Nano 2018, 3, 9–27. [CrossRef]

17. Wang, C.X.; Wu, J.P.; Jiang, K.L.; Humphrey, M.G.; Zhang, C. Stable Ag nanoclusters-based nano-sensors: Rapid sonochemical synthesis and detecting Pb²⁺ in living cells. Sens. Actuators B Chem. 2017, 238, 1136–1143. [CrossRef]

18. Li, S.X.; Chen, D.J.; Zheng, F.Y.; Zhou, H.F.; Jiang, S.X.; Wu, Y.J. Water-Soluble and Lowly Toxic Sulphur Quantum Dots. Adv. Funct. Mater. 2015, 24, 7133–7138. [CrossRef]

19. Duan, Y.X.; Tan, J.S.; Huang, Z.M.; Deng, Q.M.; Liu, S.J.; Wang, G.; Li, L.G.; Zhou, L. Facile synthesis of carboxymethyl cellulose sulfur quantum dots for live cell imaging and sensitive detection of Cr(VI) and ascorbic acid. Carbohydr. Polym. 2020, 249, 116882. [CrossRef]

20. Gao, P.X.; Wang, G.; Zhou, L. Luminescent Sulfur Quantum Dots: Synthesis, Properties and Potential Applications. ChemPhotoChem 2020, 4, 5235–5244. [CrossRef]
21. Lei, J.H.; Huang, Z.M.; Gao, P.X.; Sun, J.H.; Zhou, L. Polyvinyl Alcohol Enhanced Fluorescent Sulfur Quantum Dots for Highly Sensitive Detection of Fe\(^{3+}\) and Temperature in Cells. *Part. Part. Syst. Charact.* 2021, 38, 2000332. [CrossRef]

22. Li, X.Q.; Li, M.Q.; Chen, Y.Z.; Qiao, G.X.; Liu, Q.; Zhou, Z.; Liu, W.Q.; Wang, Q.M. Chemical sensing failed by aggregation-caused quenching? A case study enables liquid/solid two-phase determination of N\(_2\)H\(_4\). *Chem. Eng. J.* 2021, 415, 128975. [CrossRef]

23. Li, D.D.; Zhang, Y.P.; Fan, Z.Y.; Chen, J.; Yu, J.H. Coupling of chromophores with exactly opposite luminescence behaviours in mesostructured organosilicas for high-efficiency multicolour emission. *Chem. Sci.* 2015, 6, 6097–6101. [CrossRef]

24. Li, D.H.; Liu, L.; Yang, H.G.; Ma, J.; Wang, H.L.; Fan, J.M. A novel dual-response triphenylamine-based fluorescence sensor for special detection of hydrazine in water. *Mater. Sci. Eng. B Adv.* 2022, 276, 115556. [CrossRef]

25. Xie, Y.; Yan, L.Q.; Tang, Y.J.; Tang, M.H.; Wang, S.Y.; Bi, L.; Sun, W.Y.; Li, J.P. A Smart Fluorescent Probe Based on Salicylaldehyde Schiff’s Base with AIE and ESIPT Characteristics for the Detections of N\(_2\)H\(_4\) and ClO\(^-\). *J. Fluoresc.* 2019, 29, 399–406. [CrossRef] [PubMed]

26. Kong, X.Q.; Li, M.; Zhang, Y.Y.; Yin, Y.G.; Lin, W.Y. Engineering an AIE N\(_2\)H\(_4\) fluorescent probe based on alpha-cyanostilbene derivative with large Stokes shift and its versatile applications in solution, solid-state and biological systems. *Sens. Actuators B Chem.* 2021, 329, 129232. [CrossRef]

27. Wu, H.; Wang, Y.; Wu, W.N.; Xu, Z.Q.; Xu, Z.H.; Zhao, X.L.; Fan, Y.C. A novel ‘turn-on’ coumarin-based fluorescence probe with aggregation-induced emission (AIE) for sensitive detection of hydrazine and its imaging in living cells. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2019, 222, 117272. [CrossRef]

28. Chen, Z.Z.; Deng, Y.H.; Zhang, T.; Dong, W.K. A novel bifunctional-group salamo-like multi-purpose dye probe based on ESIPT and RAHB effect: Distinction of cyanide and hydrazine through optical signal differential protocol. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc.* 2021, 262, 120084. [CrossRef]

29. Li, X.; Yin, J.W.; Liu, W.Y.; Yang, Y.T.; Xu, W.Z.; Li, W. A Novel Double Fluorescence-Suppressed Probe for the Detection of Hydrazine. *ChemistrySelect* 2020, 4, 14069–14074. [CrossRef]

30. Chen, Z.; Zhong, X.X.; Qu, W.B.; Shi, T.; Liu, H.; He, H.P.; Zhang, X.H.; Wang, S.F. A highly selective HBT-based “turn-on” fluorescent probe for hydrazine detection and its application. *Tetrahedron Lett.* 2017, 58, 2596–2601. [CrossRef]

31. Jiang, X.Z.; Zhen, L.; Mingqin, S.G.; Yi, S.L.; Zeng, X.Y.; Zhang, Y.L.; Hou, L.X. A fluorescence “turn-on” sensor for detecting hydrazine in environment. *Microchem. J.* 2020, 152, 104376. [CrossRef]

32. Das, A.K.; Goswami, S. 2-Hydroxy-1-naphthaldehyde: A versatile building block for the development of sensors in supramolecular chemistry and molecular recognition. *Sens. Actuators B Chem.* 2017, 245, 1062–1125. [CrossRef]

33. Ping, Y.; David, R.W. Calculation for Fluorescence Modulation by Absorbing Species and Its Application to Measurements Using Optical Fibers. *Anal. Chem.* 1987, 59, 2391–2394.

34. Wang, H.G.; Wang, Z.G.; Xiong, Y.; Kershaw, S.V.; Li, T.Z.; Wang, Y.; Zhai, Y.Q.; Rogach, A.L. Hydrogen Peroxide Assisted Synthesis of Highly Luminescent Sulfur Quantum Dots. *Angev. Chem. Int. Ed.* 2019, 58, 7040–7044. [CrossRef] [PubMed]

35. He, Y.; Huang, W.; Liang, Y.; Yu, H.L. A low-cost and label-free assay for hydrazine using MnO\(_2\) nanosheets as colorimetric probes. *Sens. Actuators B Chem.* 2015, 220, 927–931. [CrossRef]

36. He, L.Y.; Lu, Y.X.; Wang, F.Y.; Jing, W.J.; Chen, Y.; Liu, Y.Y. Colorimetric sensing of silver ions based on glutathione-mediated MnO\(_2\) nanosheets. *Sens. Actuators B Chem.* 2018, 254, 468–474. [CrossRef]

37. Amjadi, M.; Hallaj, T.; Kouhi, Z. An enzyme-free fluorescent probe based on carbon dots-MnO\(_2\) nanosheets for determination of uric acid. *J. Photochem. Photobiol. A Chem.* 2018, 356, 603–609. [CrossRef]

38. Zhang, Y.Y.; Li, Y.X.; Zhang, C.Y.; Zhang, Q.F.; Huang, X.A.; Yang, M.D.; Shahzad, S.A.; Lo, K.K.W.; Yu, C.; Jiang, S.C. Fluorescence turn-on detection of alkaline phosphatase activity based on controlled release of PEI-capped Cu nanoclusters from MnO\(_2\) nanosheets. *Anal. Bioanal. Chem.* 2017, 409, 4771–4778. [CrossRef]

39. Zhang, Y.; Liu, J.F.; Yi, R.H.; Ai, S.F.; Cheng, H.R.; Jia, W.Z. Synthesis and Application of a Flavone-based Fluorescent Probe for Detection of Hydrazine. *Chin. J. Anal. Chem.* 2019, 46, 511–516.

40. Jiang, Q.; Wang, Z.L.; Li, M.X.; Song, J.; Yang, Y.Q.; Xu, X.; Xu, H.J.; Wang, S.F. A novel dual-response fluorescent probe based on nopinone for discriminative detection of hydrazine and bisulfate from different emission channels. *Tetrahedron Lett.* 2020, 61, 152103. [CrossRef]