CdTe Quantum Dots (QDs) Based Kinetic Discrimination of Fe$^{2+}$ and Fe$^{3+}$, and CdTe QDs-Fenton Hybrid System for Sensitive Photoluminescent Detection of Fe$^{2+}$

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A method based on the quenching kinetics for the fluorescence of glutathione capped CdTe quantum dots (GSH-CdTe QDs) was developed for discriminating Fe$^{2+}$ and Fe$^{3+}$, and a GSH-CdTe QDs-Fenton hybrid system was constructed for sensitive and selective determination of Fe$^{2+}$. Although both Fe$^{2+}$ and Fe$^{3+}$ could quench the fluorescence of GSH-CdTe QDs, the quenching kinetics was quite different for Fe$^{2+}$ and Fe$^{3+}$. The fluorescence of the GSH-CdTe QDs (30 nM) was quenched by about 18% in 1 min after the addition of Fe$^{2+}$ (10 μM), and remained unchanged with further increase of reaction time. In contrast, the fluorescence intensity of the GSH-CdTe QDs decreased by about 65% in the first 5 min after the addition of Fe$^{3+}$ (10 μM), then slowly decreased by 15% in the next 25 minutes. Other transition metal ions like Cu$^{2+}$, Ni$^{2+}$, and Co$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$ also gave very different quenching kinetics of the GSH-CdTe QDs from Fe$^{2+}$. No significant effect of the capping agents (GSH, thioglycolic acid, and mercaptopropionic acid) for the QDs on the pattern of the time course of the fluorescence of the QDs for Fe$^{2+}$ or Fe$^{3+}$ was observed. To achieve selective determination of Fe$^{2+}$ in the presence of Fe$^{3+}$, trace H$_2$O$_2$ was introduced to establish a QDs-Fenton hybrid system. The Fenton reaction between Fe$^{2+}$ and H$_2$O$_2$ resulted in hydroxyl radicals which can effectively quench the fluorescence of the QDs through electron transfer from the conduction band of the QDs to the single occupied molecular orbit of hydroxyl radicals. The high redox potential of hydroxyl radicals (2.8 V) permits more effective quenching of the fluorescence of the QDs than Fe$^{2+}$. The detection limit of the developed method was 5 nM for Fe$^{2+}$. The recovery of Fe$^{2+}$ spiked in water samples ranged from 96% to 105%.

In the past decade, quantum dots (QDs) have gained great interest in both fundamental research and technical applications because of their unique size-dependent optical and electronic properties. Compared with organic dyes, QDs possess several distinct advantageous optical properties, such as greater brightness, better stability with respect to photobleaching, and narrower spectral line-width. Recently, the progress in controlled synthesis of high-quality QDs, as well as the effective surface modifications, have intrigued analytical chemists to explore QDs as promising optical labels for sensing and biosensing events.

The fluorescence property of QDs is strongly dependent on the nature of the surface states, as well as chemical/physical environment. QDs are prone to exchange electrons or energy with the complementary partners (acceptors or donors) upon excitation, which can be engineered to signal the molecular recognition process as the presence of the target analytes can be transduced into detectable fluorescence signals. Quite a few sensing schemes based on fluorescence resonant energy transfer (FRET) or photoinduced electron transfer (PET) have been developed for detecting small molecules, and for tracing biorecognition events or biocatalytic transformations. Compared with FRET based sensing schemes, those based on the PET mechanism still remains largely unexplored. Up to now, only several PET-based sensing systems have been developed primarily for small molecules such as Vitamin C, glucose, and maltose.


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as well as anions.\textsuperscript{17} Besides, PET-based sensors have been reported for detection of double-strand DNA,\textsuperscript{18} and monitoring of anticancer drug–DNA interactions\textsuperscript{7} based on luminescent QDs.

Recently, great attention has been paid to the applications of QDs as metal ion probes because of the environmental and biological importance of metal ions. In a pioneering work on the use of luminescent QDs as selective ion probes in aqueous samples, the effect of three different ligands (l-cysteine, thioglyceral, and polyphosphate) on the luminescence deactivation of water-soluble CdS QDs with respect to several cations was investigated, including Zn\textsuperscript{2+} and Cu\textsuperscript{2+}, and the fluorescence intensity of thioglyceral-coated CdS QDs was found to be quenched selectively by Cu\textsuperscript{2+}.\textsuperscript{19} Penta-peptide (Gly-His-Leu-Leu-Cys) coated CdS QDs were reported for selective optical detection of Cu\textsuperscript{2+} and Ag\textsuperscript{+}.\textsuperscript{20} Besides fluorescence quenching, transition metal ion (Ag\textsuperscript{+}) was found to be able to activate QDs, and a fluorescence-enhancement assay for Ag\textsuperscript{+} based on water-soluble CdS QDs modified with l-cysteine was developed.\textsuperscript{21}

Depending on the nature of QDs as well as surface coatings, a number of QDs-based probes were developed for transition metal ions,\textsuperscript{22} including Hg\textsuperscript{2+},\textsuperscript{23,24} Cu\textsuperscript{2+},\textsuperscript{25,26} Ag\textsuperscript{+},\textsuperscript{27,28} and Pb\textsuperscript{2+}.\textsuperscript{29,30} Very recently, surface-engineered QDs were reported for the recognition of metal ions, and the fluorescence of the QDs was selectively modulated upon addition of target metal ions.\textsuperscript{31–33} Nevertheless, very little attention has been paid to the fluorescence behavior of QDs in the presence of various chemical species of an element.\textsuperscript{34}

Herein, we report the fluorescence behaviors of glutathione capped CdTe QDs (GSH-CdTe QDs) in the presence of different chemical species of an element. Fe\textsuperscript{2+} and Fe\textsuperscript{3+} were selected as the target metal ion pairs since both of the species are cations and also are the most common and important ion pairs in environmental and biological systems. The environmental and biological availability of iron depends largely on its valence state. Iron is also a significant factor in the evaluation of water quality, and its reactivity also drives numerous chemical processes in natural waters. In the present study, a QDs based fluorescent approach was developed to discriminate Fe\textsuperscript{2+} and Fe\textsuperscript{3+} based on their induced quenching kinetics of GSH-CdTe QDs, and a QDs-Fenton hybrid system was designed for simple and sensitive photoluminescent detection of Fe\textsuperscript{2+} with a detection limit of 5 nM.

**EXPERIMENTAL SECTION**

**Materials and Chemicals.** All reagents used were of analytical grade. CdCl\textsubscript{2}·2.5H\textsubscript{2}O, Te powder (Guoyao Chemicals Co., Shanghai, China), and KBr\textsubscript{2} (Fuchen Chemicals Co., Tianjin, China) were used to prepare CdTe QDs. Reduced glutathione (GSH) (Newprobe Biotechnology Co., Beijing, China) was used as the capping agent. Tris (Tianjin Guangfu Chemical Co., Tianjin, China). Ultrapure water (18.2 M\textsubscript{2} cm) was obtained from a WaterPro water purification system (Labconco Corporation, Kansas City, MO, U.S.A.). Aqueous solutions of Fe\textsuperscript{2+}, Fe\textsuperscript{3+}, K\textsuperscript{+}, Na\textsuperscript{+}, Ca\textsuperscript{2+}, Mg\textsuperscript{2+}, Al\textsuperscript{3+}, Mn\textsuperscript{2+}, Co\textsuperscript{2+}, Ni\textsuperscript{2+}, Cu\textsuperscript{2+}, and Zn\textsuperscript{2+} were prepared from FeSO\textsubscript{4}·7H\textsubscript{2}O, FeCl\textsubscript{3}·6H\textsubscript{2}O, KNO\textsubscript{3}, NaCl, Ca(NO\textsubscript{3})\textsubscript{2}·4H\textsubscript{2}O, MgCl\textsubscript{2}·6H\textsubscript{2}O, Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, MnCl\textsubscript{2}·4H\textsubscript{2}O, CoCl\textsubscript{2}·6H\textsubscript{2}O, NiCl\textsubscript{2}·6H\textsubscript{2}O, CuCl\textsubscript{2}·2H\textsubscript{2}O, and Zn(NO\textsubscript{3})\textsubscript{2}·7H\textsubscript{2}O, respectively.

**Apparatus.** Fluorescence measurements were performed on an F-4500 spectrofluorometer (Hitachi, Japan) equipped with a plotter unit and a quartz cell (1 cm × 1 cm). The fluorescent emission spectra were recorded in the wavelength range of 520–720 nm upon excitation at 380 nm. The slit width of excitation and emission was 5 and 10 nm, respectively. The photomultiplier tube (PMT) voltage was set at 700 V. Absorption spectra were recorded on a Shimadzu UV-3600 UV–vis–NIR spectrophotometer.

**Synthesis of the Water-Soluble GSH-CdTe QDs.** GSH-CdTe QDs were synthesized in aqueous solution based on a previous publication with minor modifications.\textsuperscript{35} In a typical synthesis, 0.2 mmol of CdCl\textsubscript{2}·2.5H\textsubscript{2}O and 0.24 mmol of GSH were mixed in a three-necked flask to form the cadmium precursor (50 mL).

The mixture was adjusted to pH 11 with 1 M NaOH, and stirred under vigorous stirring, and the solution was heated at 100 °C for various periods of time to obtain different sized GSH-CdTe QDs. The obtained GSH-CdTe QDs were precipitated with ethanol, and separated by centrifugation. Finally, the purified GSH-CdTe QDs were redispersed in the Tris-HCl buffer solution (10 mM, pH 7.4). The size and concentration of the GSH-CdTe QDs were calculated according to Peng and coworkers.\textsuperscript{36}

**Fluorescence Experiments.** For discrimination of Fe\textsuperscript{2+} and Fe\textsuperscript{3+}, to a 10 mL calibrated test tube were added 100 µL of 3.04 µM GSH-CdTe QDs, 1 mL of 0.1 M Tris-HCl buffer solution (pH 7.4), and Fe\textsuperscript{2+} or Fe\textsuperscript{3+} standard solution. The mixture was adjusted to pH 11 with 1 M NaOH, and stirred under argon for 30 min. Subsequently, 0.4 mL of freshly prepared 0.1 M KH\textsubscript{2}Te aqueous solution from KBr\textsubscript{2} and Te powder was injected into the reaction system by a syringe under vigorous stirring, and the solution was heated at 100 °C for various periods of time to obtain different sized GSH-CdTe QDs. The obtained GSH-CdTe QDs were precipitated with ethanol, and separated by centrifugation. Finally, the purified GSH-CdTe QDs were redispersed in the Tris-HCl buffer solution (10 mM, pH 7.4). The size and concentration of the GSH-CdTe QDs were calculated according to Peng and coworkers.\textsuperscript{36}
mixture was diluted to volume with ultrapure water, mixed thoroughly, and immediately scanned by F-4500 spectrophotometer. The fluorescence intensity was recorded every 1 min for a total time of 30 min to observe their quenching kinetics. The interaction kinetics of other transition metal ions was also monitored, and the procedures were similar to that of Fe$^{2+}$ or Fe$^{3+}$.

For the determination of Fe$^{2+}$, to a 10 mL calibrated test tube were sequentially added 100 μL of 3.04 μM GSH-CdTe QDs, 1 mL of 0.1 M Tris-HCl buffer solution (pH 7.4), 100 μL of 1 mM H$_2$O$_2$, and standard solution of Fe$^{3+}$ or 1 mL of water sample solution. The mixture was then diluted to volume with ultrapure water and mixed thoroughly. After incubation for 15 min, the fluorescence spectra of the QDs were recorded upon excitation at 380 nm. The fluorescence intensity at the maximum fluorescence wavelength was used for quantification.

Water Samples. Two tap water and four river water samples were collected locally. All water samples were filtered through 0.45 µm Supor filters, and analyzed immediately after sampling. For analysis, tap water and river water samples were subjected to 10- and 20-fold dilution, respectively.

RESULTS AND DISCUSSION

Characterization of the GSH-CdTe QDs. GSH-capped CdTe QDs were prepared based on a previously published method with molar ratio of 1:2:1:0.2 (GSH/Cd/Te). The precursors were converted to CdTe nanocrystals by refluxing the reaction temperature at 100 °C. We prepared a size series of CdTe QDs by changing reaction time to study the effect of the size of QDs on the analytical performance. The as-prepared CdTe-CdTe QDs with different reaction times of 15, 30, 45, 60, 75, 90, and 115 min gave the first excitonic absorption at 520.8, 538.4, 548.6, 557, 563.6, 569.4, 575.8 nm, respectively, and the maximum fluorescence emission peaks were located at 560, 584, 597, 607, 615, 622, and 631 nm, respectively (See Supporting Information, Figure S1). The size of the CdTe-CdTe QDs prepared with different reaction times of 15, 30, 45, 60, 75, 90, and 115 min was calculated to be 2.82, 3.10, 3.23, 3.31, 3.37, 3.42, and 3.44 nm, respectively, based on the UV–vis absorption spectra of the QDs according to Peng and co-workers. Except the investigation of size effect, 3.4 nm-sized QDs (reflux time of 75 min) were used for all other studies carried out in this work.

The as-prepared CdTe-CdTe QDs were water-soluble and stable in water for more than 6 months without notable precipitation in the dark under ambient conditions. The concentration-dependent fluorescent spectra of CdTe-CdTe QDs show that no emission wavelength shift was observed even at the lowest concentration of CdTe-CdTe QDs (See Supporting Information, Figure S2), suggesting that CdTe-CdTe QDs were equally dispersed in water in a large concentration range.

Discrimination of Fe$^{2+}$ and Fe$^{3+}$ Based on the Fluorescence Quenching Kinetics of the GSH-CdTe QDs. Though QDs based probes for transition metal ions have been extensively studied, very little information on the interaction between different chemical species of an element (for example, Fe$^{2+}$ and Fe$^{3+}$) and QDs is available. In this work, we found that Fe$^{2+}$ and Fe$^{3+}$ induced different quenching kinetics of GSH-CdTe QDs although both Fe$^{2+}$ and Fe$^{3+}$ could quench the fluorescence of GSH-CdTe QDs. The time course of the fluorescence of the GSH-CdTe QDs in the presence of Fe$^{3+}$ or Fe$^{2+}$ is illustrated in Figure 1. The fluorescence of the GSH-CdTe QDs was quenched by about 18% in one minute after the addition of Fe$^{3+}$ (10 μM), and remained unchanged with further increase of reaction time, indicating that it was very fast to reach equilibrium for the interaction between Fe$^{2+}$ and the GSH-CdTe QDs. For other transition metal ions of Cu$^{2+}$, Ni$^{2+}$, and Co$^{2+}$, Zn$^{2+}$, and Mn$^{2+}$, it was also very fast to reach equilibrium for their interactions with the GSH-CdTe QDs (See Supporting Information, Figure S3). In contrast, the fluorescence intensity of the GSH-CdTe QDs decreased by about 65% in the first 5 min after the addition of Fe$^{2+}$ (10 μM), then slowly decreased by 15% in the next 25 minutes. The main mechanism of fluorescence quenching of QDs by metal ions is most probably related to the transfer of electrons from the photoexcited QDs to the cation bound at its surface, and the formation of new non-radiative surface channels for electron annihilation which effectively competes with the radiative electron–hole recombination within the QDs, leading to the luminescence quenching. Thus, the observed different quenching behaviors of metal ions for the CdTe QDs most likely result from the different electronic structures and redox potentials of the metal ions.

To examine the effect of capping agents for the QDs on the quenching behavior of Fe$^{2+}$ and Fe$^{3+}$, other thiol-capped CdTe QDs, that is, thioglycolic acid and mercaptopropionic acid capped CdTe QDs were prepared according to Gaponik et al. No significant effect of the capping agents on the pattern of the time course of the fluorescence of the QDs for Fe$^{2+}$ or Fe$^{3+}$ was observed (See Supporting Information, Figure S4).

We also monitored the quenching effect of Fe$^{3+}$ and Fe$^{2+}$ (10 μM) on the fluorescence of GSH-CdTe QDs in a simulated sample matrix (K$^+$, Na$^+$, Ca$^{2+}$, Mg$^{2+}$, total 50 μM). The result showed that the quenching behavior of Fe$^{2+}$ and Fe$^{3+}$ was not affected by the co-existing ions of K$^+$, Na$^+$, Ca$^{2+}$, and Mg$^{2+}$ (See Supporting Information, Figure S5). On the basis of the above findings, Fe$^{2+}$ and Fe$^{3+}$ can be discriminated based on their different quenching kinetics of the QDs.

Fluorescence Quenching of GSH-CdTe QDs by Fe$^{2+}$ in the Presence of Trace H$_2$O$_2$. Though Fe$^{2+}$ and Fe$^{3+}$ can be discriminated based on their quenching kinetics, selective detection of Fe$^{2+}$ or Fe$^{3+}$ with GSH-CdTe QDs is impossible as both iron species can quench the fluorescence of the QDs. For this reason, further efforts are necessary to reduce the interspecies interference. It is well-known that in the presence of Fe$^{2+}$, H$_2$O$_2$ can generate hydroxyl radicals with strong oxidizing nature, which is called Fenton reaction, and is widely applied in wastewater treatment.\(^{39,40}\) Because of the lack of the information on the interaction of hydroxyl radicals with QDs, we investigated the quenching effect of hydroxyl radicals on the fluorescence of QDs. The concentrations of Fe$^{2+}$ and H$_2$O$_2$ were set at very low levels to ensure that individual Fe$^{2+}$ or H$_2$O$_2$ caused negligible influence on the fluorescence intensity of QDs. It was found that the generated hydroxyl radicals from H$_2$O$_2$ and Fe$^{2+}$ quenched the fluorescence of GSH-CdTe QDs to a much larger extent than individual H$_2$O$_2$ or Fe$^{2+}$ (Figure 2). Gill et al.\(^{41}\) reported that 1 mM H$_2$O$_2$ quenched about 40% of the fluorescence of mercaptoundecanoic acid capped CdSe@ZnS QDs in 10 min. Our experiments showed that 7 \(\mu\)M Fe$^{2+}$ reduced 50% of the fluorescence intensity of GSH-CdTe QDs in 5 min. However, 0.1 \(\mu\)M Fe$^{2+}$ in the presence of 10 \(\mu\)M H$_2$O$_2$ quenched about 45% of the fluorescence of GSH-CdTe QDs in 10 min. No such effects were observed when Fe$^{3+}$ was used to replace Fe$^{2+}$. The above results indicate that a selective and sensitive detection of Fe$^{2+}$ based on the GSH-CdTe QDs-Fenton hybrid system is feasible.

In the presence of Fe$^{2+}$ and H$_2$O$_2$, hydroxyl radicals are generated according to the following reaction:\(^{42}\)

\[
\text{H}_2\text{O}_2 + \text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + \text{OH}^- + \cdot \text{OH} \tag{1}
\]

Hydroxyl radical is an important active oxygen-containing species with a redox potential of 2.8 V (vs standard hydrogen electrode, SHE), and has extremely strong ability to capture electron.\(^{43}\) The redox potential of the conduction band of the GSH-CdTe QDs measured by cyclic voltammetry,\(^{44}\) is -1.15 V (See Supporting Information, Figure S6). Thus, the redox potential of the hydroxyl radical is high enough to induce thermodynamic electron transfer from the conduction band of CdTe QDs to the unoccupied band of the hydroxyl radicals (Figure 3):

\[
\cdot \text{OH} + e^- \rightarrow \text{OH}^- \tag{2}
\]

Besides, all the reactants and products for Fenton reaction have negligible absorption bands, and thus the energy transfer mechanism can be ruled out as no spectral overlap between these substances and the QDs is possible. Since the contribution from individual 0.1 \(\mu\)M Fe$^{2+}$ or 10 \(\mu\)M H$_2$O$_2$ to the fluorescence quenching of the QDs is negligible (Figure 2), we suppose that the electron transfer from the traps of the QDs to hydroxyl radicals led to the fluorescence quenching.

The schematic for the fluorescence quenching of the QDs by hydroxyl radicals is illustrated in Figure 3A. Two pathways may account for the electron transfer: the electrons at the conductive band, and Cd-defect-related band to the half-filled singly occupied molecular orbital (SOMO) of the hydroxyl radicals (Figure 3B). These processes led to significant quenching of the fluorescence of the QDs (Figure 2). Particularly, because of the strong oxidizing nature of the hydroxyl radicals, the fluorescence quenching can be achieved at extremely low level of Fe$^{2+}$, thus providing a sensitive approach for Fe$^{2+}$ detection.

Reactive oxygen species have been reported to etch the lattice of QDs, resulting in blue-shift of the fluorescence peak position of QDs.\(^{45-47}\) In the present work, fluorescence quenching by the hydroxyl radicals led to no shift of the fluorescence peak position of GSH-CdTe QDs and unchanged first excitonic absorption peak of GSH-CdTe QDs, even when the fluorescence of the QDs was very weak upon quenching by the hydroxyl radicals. These results ruled out the oxidative etching mechanism, and further supported the electron-transfer hypothesis. It should be noted that oxidative etching of QDs often requires high concentrations of oxidants\(^{47}\) or long time for etching.\(^{43}\) In this work, the concentration of hydroxyl radicals generated by Fenton reaction was extremely low, and capturing the electron from the conduction band and Cd-defect-related band by hydroxyl radicals might dominate the quenching process.

**Factors Affecting the Sensitivity of the QDs-Fenton Hybrid System for Optical Detection of Fe$^{2+}$.** Figure 4 illustrates the quenching efficiency of Fe$^{2+}$ (0.1 \(\mu\)M) in the presence of H$_2$O$_2$ (10 \(\mu\)M) as a function of the concentration of GSH-CdTe QDs. The quenching efficiency decreased rapidly with increasing concentration of the QDs because the fluorescence intensity significantly increased with the concentration of the QDs. For other measurements, 30 nM of GSH-CdTe QDs was used. At

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of 10 \( \mu M \) GSH-CdTe QDs was tested with 0.1 \( \mu M \) Fe\(^{2+}\) in the absence of Fe\(^{2+}\) and \( \text{H}_2\text{O}_2 \). All measurements were carried out in Tris-HCl buffer solution (pH 7.4, 10 mM). This concentration, the absorbance of the QD solution was less than 0.01, thus the possible self-absorption and inner filter effect in the fluorescence measurements were minimized.

The effect of pH on the quenched fluorescence intensity of 30 nM GSH-CdTe QDs was tested with 0.1 \( \mu M \) Fe\(^{2+}\) in the presence of 10 \( \mu M \) \( \text{H}_2\text{O}_2 \). Because the QDs were unstable in acidic media, pH lower than 6 was not considered. In the studied pH range of 6.0–10.5, the fluorescence intensity of the QDs gradually increased in the absence of Fe\(^{2+}\) and \( \text{H}_2\text{O}_2 \), but the quenched fluorescence intensity with 0.1 \( \mu M \) Fe\(^{2+}\) in the presence of 10 \( \mu M \) \( \text{H}_2\text{O}_2 \) reached the maximum in the pH range of 6.0–7.5 (See Supporting Information, Figure S7). To keep the QDs as stable as possible and to ensure sensitive determination of Fe\(^{2+}\), a Tris-HCl buffer solution (pH 7.4, 10 mM) was used.

Different sized CdTe QDs were prepared by changing the reflux time to study the effect of the size of the QDs. No significant effect of the size of GSH-CdTe QDs on the quenched fluorescence intensity was observed in the presence of 0.1 \( \mu M \) Fe\(^{2+}\) and 10 \( \mu M \) \( \text{H}_2\text{O}_2 \) (See Supporting Information, Figure S8). For all other experiments, 3.4 nm-sized QDs (reflux time of 75 min) were used because of their best optical properties with a maximum fluorescence wavelength of >600 nm (the common background fluorescence of water sample matrix was below 600 nm).

The effect of \( \text{H}_2\text{O}_2 \) concentration on the quenched fluorescence intensity of GSH-CdTe QDs (3.4 nm, 30 nM) was tested with 0.1 \( \mu M \) Fe\(^{2+}\). No obvious change of the quenched fluorescence intensity of GSH-CdTe QDs was observed in the studied \( \text{H}_2\text{O}_2 \) concentration range of 1–20 \( \mu M \) (See Supporting Information, Figure S9). \( \text{H}_2\text{O}_2 \) concentration higher than 20 \( \mu M \) was not tested as \( \text{H}_2\text{O}_2 \) itself induced detectable quenching effect toward QDs. Therefore, 10 \( \mu M \) \( \text{H}_2\text{O}_2 \) solution was employed.

**Figures of Merit for the Proposed QDs-Fenton Hybrid System Based Fluorescent Detection of Fe\(^{2+}\)** The fluorescence quenching was best described by the Stern–Volmer equation (Figure 5, inset):

\[
F_0/F = 1 + K_{SV}C
\]

where the \( F_0 \) is the initial fluorescence intensity of the QDs in the absence of analyte, \( F \) is the fluorescence intensity in the presence of analyte, \( K_{SV} \) is the Stern–Volmer quenching constant, which is related to the quenching efficiency, and \( C \) is the concentration of analyte. Figure 5 shows the Fe\(^{2+}\) concentration-dependent quenching of the fluorescence intensity of the QDs, and the inset in Figure 5 gives the Stern–Volmer plots for Fe\(^{2+}\). A linear calibration plot was observed in the range of 0.01–1 \( \mu M \) with a correlation coefficient of 0.9950 and a linear regression equation of \( F_0/F = 1.70C + 1.1 \) (where \( C \) is the concentration of Fe\(^{2+}\) in \( \mu M \)). The detection limit (3\( \sigma \)) for Fe\(^{2+}\) was 5 nM, and the precision for 11 replicate measurements of 0.1 \( \mu M \) Fe\(^{2+}\) was 2.5% (RSD).

To evaluate the selectivity of the proposed QDs-Fenton hybrid system based fluorescent probe, the effect of various co-existing metal cations on the quenched fluorescent intensity of GSH-CdTe QDs (3.4 nm, 30 nM) by 0.1 \( \mu M \) Fe\(^{2+}\) in the presence of 10 \( \mu M \) \( \text{H}_2\text{O}_2 \) was examined (Table 1). The quenched fluorescent intensity of GSH-CdTe QDs (3.4 nm, 30 nM) by 0.1 \( \mu M \) Fe\(^{2+}\) was unaffected by 10000-fold excess of K\(^+\) and Na\(^+\), 2500-fold of...
Ca$^{2+}$ and Mg$^{2+}$, 1000-fold of Al$^{3+}$, and 25-fold of Fe$^{3+}$. The tolerant concentrations for transition metal ions were much lower than those of alkali and alkali-earth metal ions. For the common transition metal ions, the selectivity of the QD-Fenton hybrid system depends not only on the selectivity of Fenton reaction itself, but also on the potential for direct interaction with the QDs. For example, transition metal ions, such as Mn$^{2+}$, Ni$^{2+}$, and Co$^{2+}$, can also participate in “Fenton-like” reactions, but their ability to induce the generation of hydroxyl radical was much lower than that of Fe$^{2+}$. In addition, these transition metal ions can directly quench the fluorescence of QDs and thus the QD-hybrid system. However, as the average concentrations of these co-existing metal ions in a river water matrix do not exceed the tolerant concentrations (See Supporting Information, Table S1), no significant interference from these co-existing metal ions in river water samples is expected for the detection of Fe$^{2+}$.

**Determination of Fe$^{2+}$ in Water Samples.** The proposed QDs-Fenton hybrid system based fluorescent probe was applied to the determination of trace Fe$^{2+}$ in water samples. Two tap water and four river water samples were collected locally and analyzed for Fe$^{2+}$. Background fluorescence of the water matrix was observed below 560 nm, but it showed minimal influence in the measurement wavelength range after 10–20 fold dilution. As shown in Table 2, the quantitative spike-recoveries ranged from 96% to 105%, and the determined concentrations of Fe$^{2+}$ by the developed method agreed with those by an independent method based on flow injection online knotted reactor sorption preconcentration and separation coupled with ICPMS (FI-KR-ICPMS). These results demonstrate the potential usefulness of proposed QDs-Fenton hybrid system based fluorescent probe for selective detection of Fe$^{2+}$ in real water samples.

**CONCLUSIONS**

We have developed a method for discriminating Fe$^{2+}$ and Fe$^{3+}$ based on their quenching kinetics for the fluorescence of GSH-CdTe QDs. We have also proposed a GSH-CdTe QDs-Fenton hybrid system for sensitive and selective determination of trace Fe$^{2+}$ based on the fact that Fe$^{2+}$ can catalytically induce the generation of hydroxyl radicals from H$_2$O$_2$ and hydroxyl radicals can quench the fluorescence of GSH-CdTe QDs more effectively than individual Fe$^{2+}$ or H$_2$O$_2$. As the QDs-Fenton hybrid system provides high sensitivity toward Fe$^{2+}$, interference from Fe$^{3+}$ and other transition metal ions is significantly reduced. The present approach provides a new protocol for selective recognition and probing of iron species without the need for extra functionalization/immobilization steps for QDs.

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**SUPPORTING INFORMATION AVAILABLE**

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Table 1. Effect of Co-Existing Ions on the Detection of 0.1 μM Fe$^{2+}$ by the Proposed QDs-Fenton Hybrid System Based Fluorescent Probe

<table>
<thead>
<tr>
<th>metal ion</th>
<th>concentration/μM</th>
<th>quenched fluorescence change/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$^{+}$</td>
<td>1000</td>
<td>-3.1</td>
</tr>
<tr>
<td>Na$^{+}$</td>
<td>1000</td>
<td>+2.2</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>250</td>
<td>-1.0</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>250</td>
<td>-3.7</td>
</tr>
<tr>
<td>Al$^{3+}$</td>
<td>100</td>
<td>-3.0</td>
</tr>
<tr>
<td>Zn$^{2+}$</td>
<td>50</td>
<td>-2.0</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>5</td>
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<tr>
<td>Mn$^{2+}$</td>
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<tr>
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<tr>
<td>Cu$^{2+}$</td>
<td>0.1</td>
<td>-4.4</td>
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</tbody>
</table>

Table 2. Analytical Results for the Detection of Fe$^{2+}$ in Water Samples

<table>
<thead>
<tr>
<th>sample</th>
<th>found by this method $(mean \pm σ, n = 3)/μM$</th>
<th>recovery $(mean \pm σ, n = 3)/%$</th>
<th>found by FI-KR-ICPMS$^{51}$ $(mean \pm σ, n = 3)/μM$</th>
</tr>
</thead>
<tbody>
<tr>
<td>tap water 1</td>
<td>0.114 ± 0.020</td>
<td>96 ± 4</td>
<td>0.124 ± 0.019</td>
</tr>
<tr>
<td>tap water 2</td>
<td>0.170 ± 0.024</td>
<td>103 ± 4</td>
<td>0.185 ± 0.027</td>
</tr>
<tr>
<td>river water 1</td>
<td>nd$^{a}$</td>
<td>97 ± 3</td>
<td>nd</td>
</tr>
<tr>
<td>river water 2</td>
<td>nd</td>
<td>98 ± 5</td>
<td>nd</td>
</tr>
<tr>
<td>river water 3</td>
<td>105 ± 6</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>river water 4</td>
<td>102 ± 3</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

$^{a}$ nd: not detectable. For 0.20 μM Fe$^{2+}$ spiked in the water samples.