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PAPER

Detection of DNA using an “off-on” switch of regenerable biosensor based on an electron transfer mechanism from glutathione-capped CdTe quantum dots to Nile blue

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Although various strategies have been reported for double-stranded DNA (DNA) detection, development of a time-saving, specific, and regenerated fluorescence sensing platform still remains a realistic goal. In this study, we proposed a new DNA detection method replying on an “off-on” switch of a regenerated fluorescence biosensor based on an electron transfer mechanism from glutathione (GSH)-capped CdTe quantum dots (QDs) to Nile blue (NB). Initially, the high fluorescence of GSH-capped CdTe QDs could be effectively quenched by NB due to the binding of NB to the GSH on the surface of the QDs and the electron transfer from the photoexcited GSH-capped CdTe QDs to NB. Then, the high affinity of DNA to NB enabled NB to be dissociated from the surface of GSH-capped CdTe QDs to form more stable complex with DNA and suppress the electron transfer process between GSH-capped CdTe QDs and NB, thereby restoring the fluorescence of NB surface modified GSH-capped CdTe QDs (QDs-NB). In addition, we have testified the regenerability of the proposed DNA sensor. The corresponding result shows that this DNA sensor is stable over two reuses. This fluorescence “off-on” signal was sensitive to the concentration of DNA in the range from 0.0092 to 25.0 $\mu\text{g}\cdot\text{mL}^{-1}$ with a good correlation coefficient of 0.9989, and the detection limit ($3\sigma/S$) was 2.78 $\text{ng}\cdot\text{mL}^{-1}$. To further investigate perfect analysis performance, the developed biosensor was applied to the determination of DNA in human fresh serum samples with satisfactory results.

Introduction

Deoxyribonucleic acid (DNA), which serves as the carrier of genetic information and the material of gene expression, is a very important biomolecule. Due to its significant functions, the sensitive and selective detection methods of DNA have attracted considerable interest in the research on life sciences such as genetics, virology, and molecular biology¹. To date, a large number of sensitive techniques such as fluorescence², electrochemistry³, resonance Rayleigh scattering⁴, surface plasmon resonance⁵, and chemiluminescence⁶ have been developed toward DNA detection. Although these methods can detect low concentration of DNA, some inherent issues still can't be avoided, such as multiple assay steps, lack regenerability, variety of expensive characterizations, complex probe preparation, poor stability and repeatability. To avoid the limitations of these detection methods, it is imperative to search alternative ways of DNA detection in a simpler, more rapid and regenerated manner that is adaptable for both laboratory and clinical analysis.

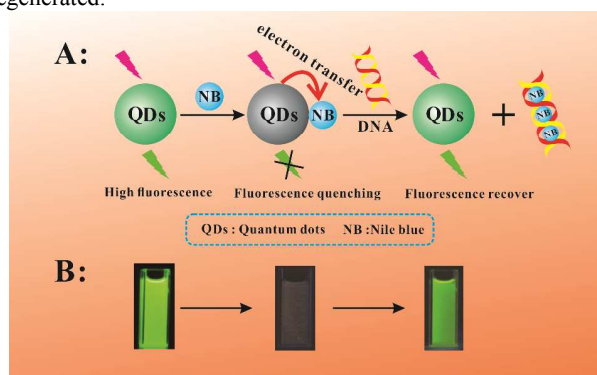
In recent years, the exploration of systems capable of sensing and recognition based on semiconductor quantum dots (QDs) is a topic of considerable interest in chemo/biosensing applications. This phenomenon is mainly originated from QDs have many merits over conventional organic and inorganic fluorophores such

as high emission quantum yield, high photobleaching threshold, excellent photostability, size-tunable photoluminescence spectra, broad absorption, and narrow emission wavelengths⁷. In addition, the large surface of QDs is favorable for attaching variable ligands and thus getting controllable properties⁸. All of these properties therefore make QDs excellent candidates for the development of novel and sensitive sensors in current research. Earlier studies related to the interactions between QDs and metal ions revealed that the surface capping ligands had a profound effect on the luminescence response of QDs to physiologically important metal cations⁹. On this basis, it can be reasonably expected that by properly choosing QDs surface ligands, specific sensing of analytes can be achieved. Thereby functionalized QDs have become one of the most important fluorescent sensors for many analytes such as ions, small molecules and biomacromolecules¹⁰.

Currently, QDs have attracted extensive application studies in biosensing field¹¹. However, most of these fluorescent sensors are based on the “turn-off” mode, where a variety of factors rather than quencher can induce the ultimate fluorescence “off” state¹². Then significant progress is made to respond to this challenge, by developing the “off-on” switch systems. In comparison with the fluorescence “turn-off” sensors, the fluorescence “off-on” mode seems to be more preferable due to the reduction of the chance of false positives. Namely, the

fluorescence “off-on” sensing systems have better selectivity than “turn-off” sensors¹³. Therefore, it would be significant to construct a novel, sensitive, specific, and regenerated assay for DNA detection based on the QDs-modified “off-on” fluorescent sensor.

In this study, we have designed a novel and reusable fluorescence “off-on” switch system for sensitive DNA detection based on electron transfer between glutathione (GSH)-capped CdTe quantum dots (QDs) and Nile blue (NB) under physiological conditions for the first time. In our experiment conditions, the oppositely charged GSH-capped CdTe QDs and NB can form assembling sensor due to electrostatic interaction, which effectively quench the fluorescence intensity of GSH-capped CdTe QDs. With the addition of DNA, NB was inclined to embed into DNA double helix structure to form more stable complex with DNA through intercalation, resulting in the attenuation on the electron transfer efficiency between GSH-capped CdTe QDs and NB, thereby restoring the fluorescence intensity of the quenched GSH-capped CdTe QDs (Scheme 1). Such combined and fluorescence could greatly improve the sensitivity of the detection system, which could specifically and selectively detect DNA in biological samples at the nanogram level. Simultaneously, this DNA sensor is regenerated, which can be stable over two reuses. In comparison with previous methods, our approach holds the advantages of simple, rapid, sensitive and regenerated.



Scheme 1 (A) Schematic illustration for the signal transduction mechanism for the developed “off-on” switching of regenerated biosensor for DNA based on electron transfer between GSH-capped CdTe QDs and NB; (B) the corresponding photographs of the “off-on” switching of regenerated biosensor under the UV lamp (excitation wavelength at 365 nm).

Experimental Section

Reagents

The main chemical reagents used in the present study were CdCl₂·2.5H₂O (Shanghai Chemicals Reagent Co., Shanghai, China), Te powder (Sinopharm Chemical Reagent Co., Shanghai, China), glutathione (GSH, Aladdin Reagent Co., Shanghai, China), Nile blue (NB, E Merck, America), NaBH₄ (Tianjin Huanwei Fine Chemical Co., Tianjin, China), and Herring sperm DNA (DNA, St. Louis, MO, USA). Yeast ribonucleic acid (RNA), bovine serum albumin (BSA), human serum albumin (HSA), and hemoglobin were purchased from Sigma (St. Louis, MO, USA). Tris-HCl buffer solutions with different pH were prepared according to suitable proportion. All reagents used were

of analytical grade without further purification. Water used throughout was doubly deionized.

Apparatus

A Hitachi F-2500 spectrofluorophotometer (Hitachi Company, Tokyo, Japan) was used to record the fluorescence and resonance Rayleigh scattering (RRS) spectra. A UV-2450 spectrophotometer (Tianmei Corporation, Shanghai, China) was applied to record the absorption spectra. Hitachi-600 transmission electron microscopy (TEM, Hitachi Company, Japan), XD-3 X-ray diffraction (XRD, Purkinje General Instrument Co., Ltd. Beijing, China) and atomic force microscope (AFM, NanoScope quadrex, veeco Corporation American, Tapping Mode, pinpoint: TESP7 Veeco) were adopted to examine the appearance and size of nanoparticles. A FL-TCSPC Fluorolog-3 fluorescence spectrometer (Horiba Jobin Yvon Inc., France) was used to measure fluorescence lifetime of GSH-capped CdTe QDs and GSH-capped CdTe QDs-NB system at room temperature (excitation/emission wavelength=350 nm/559 nm). A PHS-3C pH meter (Leici, Shanghai, China) was used to adjust the pH values of the aqueous solutions.

Synthesis of GSH-capped CdTe QDs

Aqueous colloids of GSH-capped CdTe QDs solution were prepared according to the previously described method¹⁴. Under N₂ atmosphere and magnetic stirring, tellurium powder (0.0383 g) was reacted with excessive sodium borohydride in deionized water to produce the colorless solution of sodium hydrogen telluride (NaHTe).

CdCl₂·2.5H₂O (0.1028 g) and GSH (0.1844 g) were dissolved in 150 mL deionized water. Under magnetic stirring, the pH of the mixture was adjusted to 10.5 using the dropwise addition of NaOH solution (1 mol·L⁻¹). The solution was deaerated by N₂ bubbling for about 30 min. Under stirring, H₂Te gas generated by the reaction of the solution of NaHTe with diluted H₂SO₄ (0.5 mol·L⁻¹) was passed through the oxygen-free Cd²⁺ solution together with a slow nitrogen flow. Then the resulting solution mixture was heated to 369 K and refluxed under nitrogen for 1 h. The salmon pink CdTe solution was obtained. The concentration of GSH-capped CdTe QDs was 3.0×10⁻³ mol·L⁻¹ (determined by the Cd²⁺ concentration).

General procedure

To obtain the ideal assembling sensor, 1.0 mL Tris-HCl buffer solution (0.1 mol·L⁻¹, pH 7.6; 0.013 mol·L⁻¹ NaCl), 1.0 mL above as-prepared GSH-capped CdTe QDs and an appropriate amount of NB were sequentially added to a 10.0 mL calibrated test tube. The mixture was diluted to volume with deionized water. After incubation for 10.0 min, the RRS, fluorescence and UV-vis absorption spectra of solution were examined.

To determine the DNA by this novel biosensor, 1.0 mL Tris-HCl buffer solution (0.1 mol·L⁻¹, pH 7.6; 0.013 mol·L⁻¹ NaCl), 1.0 mL above as-prepared GSH-capped CdTe QDs, and appropriate amount of NB were added into a 10.0 mL calibrated test tube, diluted with deionized water to the mark, and mixed thoroughly with gentle shaking. After incubation for 10.0 min, different concentrations of DNA were added into above system and incubated for another 10.0 min. The resulting solutions were examined by RRS, fluorescence spectroscopy.

Results and Discussion

Characterization of the synthesized GSH-capped CdTe QDs

The morphology of the as-prepared GSH-capped CdTe QDs was investigated by TEM. It is quite evident that these nanoparticles are close to spherical and are uniform with an average diameter of 3.0 nm (Figure 1A). Meanwhile, XRD spectrum of GSH-capped CdTe QDs was also analyzed. As shown in Figure 1B, the diffraction peaks were broad and weak, but the main peaks are centered at approximately $2\theta=24.60^\circ$, 38.32° and 47.01° , which basically conform to those of CdTe, centered at $2\theta=24.59^\circ$, 40.86° and 47.39° , respectively¹⁵. In addition, the (curve A) UV-vis absorption and (curve B) fluorescence emission spectra of as-prepared GSH-capped CdTe QDs were also shown in Figure 1C. The UV-vis absorption spectrum showed a strong excitonic absorption in the ultraviolet region, and the characteristic absorption peak is located at 523 nm. Meanwhile, the fluorescence emission spectrum further confirmed that GSH-capped CdTe QDs were nearly monodisperse and homogeneous because of its favorable symmetry and narrow FWHM (about 42 nm), the observed fluorescence band centered at 559 nm (excitation 350 nm)¹⁶.

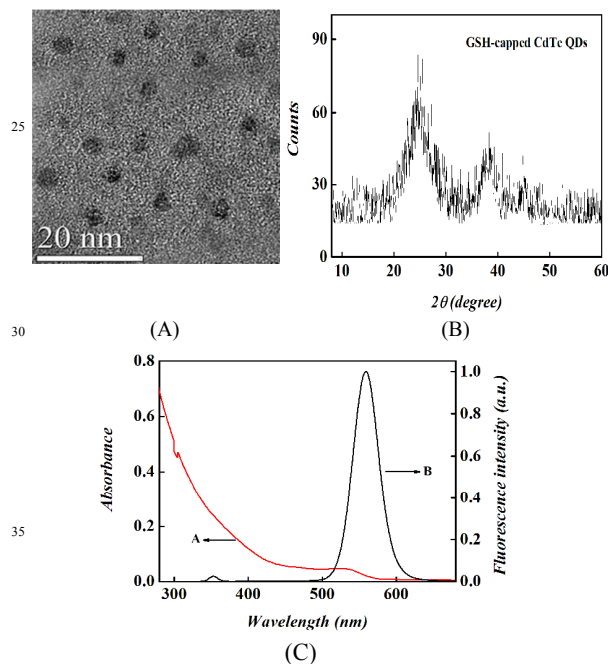


Figure 1 (A) TEM image, (B) XRD pattern of as-prepared GSH-capped CdTe QDs; (C) UV-vis absorption (curve A) and fluorescence (curve B) spectra of as-prepared GSH-capped CdTe QDs.

The construction of the assembling fluorescence sensor

In this work, the initial fluorescence spectra of GSH-capped CdTe QDs were recorded in the absence and presence of NB and shown in Figure 2. It was found that a progressive decrease in the fluorescence intensity of GSH-capped CdTe QDs was caused by NB, accompanied by a decrease of wavelength emission maximum λ_{max} (a blue shift, from 559 to 555 nm) in the GSH-capped CdTe QDs spectrum, a shift that can reasonably be attributed to an increased hydrophobicity of the region surrounding the GSH-capped CdTe QDs as a result of the

formation of GSH-capped CdTe QDs-NB complex¹⁷. The fluorescence quenching extent of GSH-capped CdTe QDs was directly proportional to the concentration of NB from 0 to $14.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$. When the concentration of NB was above $14.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ in the as-prepared GSH-capped CdTe QDs solution system, the fluorescence quenching degree of GSH-capped CdTe QDs almost remained unchanged. That is to say, the concentration of NB at $14.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ can result in the fluorescence quenching degree of GSH-capped CdTe QDs reached a limit (the quenching efficiency is 83.77%).

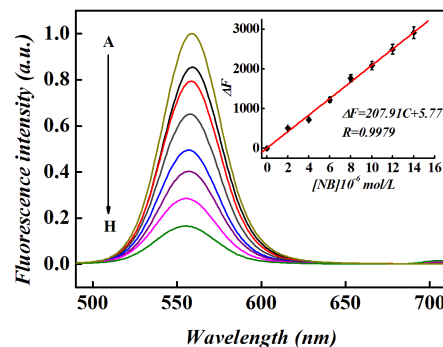


Figure 2 Fluorescence emission spectra of GSH-capped CdTe QDs in the absence and presence of NB in $0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl at $\text{pH}=7.6$; c (GSH-capped CdTe QDs) = $3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; c (NB)/($10^{-6} \text{ mol}\cdot\text{L}^{-1}$), A-H: 0.0, 2.0, 4.0, 6.0, 8.0, 10.0, 12.0, and $14.0 \text{ mol}\cdot\text{L}^{-1}$, respectively. The insert corresponds to the relationship of the decreased fluorescence intensity of GSH-capped CdTe QDs with the concentration of NB.

Quenching mechanisms of fluorescence emission from QDs are usually classified as either dynamic quenching or static quenching. To explore the mechanism of the reaction, the well-known Stern-Volmer equation played an important role in demonstrating the quenching behavior of quencher on the fluorescence of QDs¹⁸.

$$F_0/F = 1 + K_{sv} [Q] \quad (1)$$

In this expression, F_0 and F are the fluorescence intensities of GSH-capped CdTe QDs in the absence and presence of a quencher (NB), respectively; $[Q]$ is the concentration of the quencher. K_{sv} is the Stern-Volmer quenching constant, which defines the quenching efficiency of the quencher. Hence, Eq. 1 is applied to determine K_{sv} of GSH-capped CdTe QDs-NB system at four different temperatures (283 K, 288 K, 295 K and 298 K) by linear regression of a plot of F_0/F against $[Q]$ (as shown in Figure 3). The values of quenching constants (K_{sv}) are listed in Table 1. It can be seen that the Stern-Volmer quenching constant (K_{sv}) is inversely correlated with temperature, which indicates that the probable quenching mechanism is the formation of GSH-capped CdTe QDs-NB complex (static quenching) rather than by dynamic quenching¹⁹.

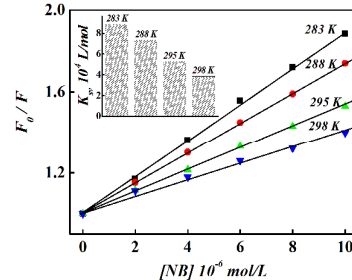


Figure 3 Stern-Volmer curves for the GSH-capped CdTe QDs-NB solution system at four different temperatures (GSH-capped CdTe QDs, $3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; Tris-HCl buffer solution, 1.0 mL, pH=7.6).

Table 1 Stern-Volmer quenching constants for the interaction of GSH-capped CdTe QDs with NB at various temperatures

pH	T/K	$K_{sv}/(10^4, \text{L}\cdot\text{mol}^{-1})$	R^a	$S.D.^b$
	283	8.95	0.9995	0.01200
7.6	288	7.38	0.9999	0.00335
	295	5.30	0.9997	0.00531
	298	3.87	0.9962	0.01412

^a R is the correlation coefficient.

^b $S.D.$ is the standard deviation for the K_{sv} values.

One additional method to distinguish static and dynamic quenching is by careful examination of the absorption spectra of the fluorophore. Dynamic quenching only affects the excited states of the fluorophores, and thus no changes in the absorption spectra are expected. In contrast, ground-state complex formation will frequently result in perturbation of the absorption spectrum of the fluorophore²⁰. For reconfirming the probable quenching mechanism of fluorescence of GSH-capped CdTe QDs caused by NB is initiated by static quenching, UV-vis absorption spectra of GSH-capped CdTe QDs-NB solution system were studied and the results were presented in Figure 4. In the spectrum of (curve A) pure GSH-capped CdTe QDs, there is strong absorption in the UV area at wavelengths <400 nm, whereas the absorption in the visible is relatively weak. The curve C is the absorption spectrum of NB with distilled water as the reference, but curve D is the absorption spectrum of NB with GSH-capped CdTe QDs as the reference. It shows that there is an obvious spectral change by comparing curve C with curve D, implying that there is strong interaction between GSH-capped CdTe QDs and NB. Namely, the quenching type is static quenching

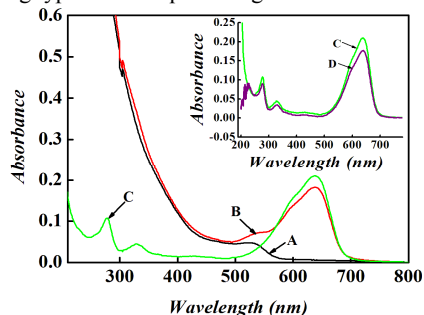


Figure 4 UV-vis absorption spectra of (A) GSH-capped CdTe QDs, (B) mixture solution system (GSH-capped CdTe QDs and NB), (C) NB (with distilled water as the reference) and (D) NB (with GSH-capped CdTe QDs as the reference) (GSH-capped CdTe QDs, $3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; NB, $4.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$; Tris-HCl buffer solution, $0.01 \text{ mol}\cdot\text{L}^{-1}$, pH=7.6).

To further confirm the quenching type, the fluorescence lifetimes of GSH-capped CdTe QDs in the absence and presence of NB were studied (as shown in Figure 5). It is well-known that the measurement of fluorescence lifetime is the most definitive method to distinguish static and dynamic quenching. The lifetime of fluorescence molecule on excited state has no change in the presence of quencher when static quenching takes place. Reversely, fluorescence lifetime has to be shorter if dynamic quenching occurs²¹. As shown in Figure 5, the fluorescence lifetimes of GSH-capped CdTe QDs in the absence and presence of NB are almost no change, which also indicates that the quenching type is static quenching. In the process of synthesis

GSH-capped CdTe QDs, large amounts of GSH can self-assemble on the surface of QDs to play a role in capping agent with amounts of amine and carboxylic groups. Under the experimental conditions ($0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl buffer solution, pH=7.6), water-soluble GSH-capped CdTe QDs carry the negatively charged carboxylic groups because the isoelectric point of GSH is 5.93. As a result, after the addition of NB solution, the positively charged NB (see Figure 6) and the negatively charged QDs form a complex due to electrostatic attraction, which resulted in the increase of the molecular volume and the enhancement of RRS intensity (see Figure 10)²². Upon photoexcitation of a QD, the electrons from the valence band are excited to the conduction band. The excited electron and the oppositely charged “hole” attract one another. When the excited electron recombines with the hole, a photon is emitted in the form of fluorescence¹⁸. In this work, NB is highly electrophilic and can work as a cationic electron acceptor. The static association of GSH-capped CdTe QDs with NB induces ultrafast photoinduced electron transfer from GSH-capped CdTe QDs to the electron acceptor, preventing the normal recombination of the electron and the hole in GSH-capped CdTe QDs, and results in a decrease of the fluorescence intensity of GSH-capped CdTe QDs. Therefore, we regarded that NB works as a quencher to the fluorescence of GSH-capped CdTe QDs through an electron transfer mechanism.

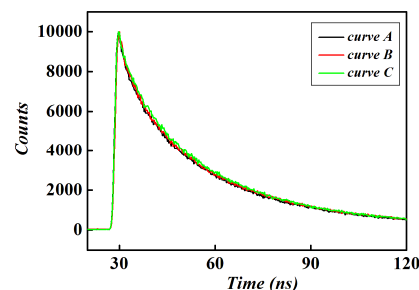


Figure 5 Effects of NB on the fluorescence lifetime of GSH-capped CdTe QDs. (curve A) GSH-capped CdTe QDs ($\tau = 32.67 \text{ ns}$); GSH-capped CdTe QDs in the presence of NB at (curve B) $5.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ ($\tau = 33.22 \text{ ns}$) and (curve C) $10.0 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ ($\tau = 33.71 \text{ ns}$). (GSH-capped CdTe QDs, $3.0 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; Tris-HCl buffer solution, 1.0 mL, pH=7.6).

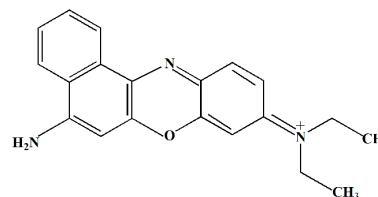


Figure 6 Molecular structure of NB.

80 Optimization of analytical conditions

(1) Effect of acidity: The pH of the solution not only affected the NB-induced the fluorescence quenching of GSH-capped CdTe QDs, but also the subsequent fluorescence recovery by DNA. In order to detect DNA with this proposed fluorescent sensor at physiological conditions, Tris-HCl buffer solution was selected to control the acidity of the GSH-capped CdTe QDs-NB-DNA system. The effect of acidity on the system was investigated from pH 6.8 to 8.0 (see Figure 7A). The experimental results showed that the suitable pH value was 7.6, which revealed a maximum

change of fluorescence intensities in the process of NB-induced the fluorescence quenching and the subsequent fluorescence recovery. To obtain a lower detection limit for DNA, the pH of the solution system used in the experiment was set at 7.6. At the same time, the effect of the dosage of Tris-HCl buffer solution on the fluorescence intensity of GSH-capped CdTe QDs-NB-DNA system was also discussed. The results showed that the optimal dosage of Tris-HCl buffer solution was 1.0 mL. That is to say, the optimum amount of Tris-HCl buffer solution was $0.01 \text{ mol}\cdot\text{L}^{-1}$.

(2) Effect of concentration of GSH-capped CdTe QDs: The influence of the concentration of GSH-capped CdTe QDs on the fluorescence intensity of GSH-capped CdTe QDs-NB system was investigated by keeping NB concentration and pH value while changing the concentration of GSH-capped CdTe QDs. The results revealed that the optimum amount of GSH-capped CdTe QDs was $3.0\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$ (see Figure 7B).

(3) Effect of reaction time: The influence of reaction time on the fluorescence intensity of GSH-capped CdTe QDs-NB system was studied. The results demonstrated that the reaction finished within 10.0 min and the fluorescence intensity was stable more than 120 min. The time scale of 10.0 min was also adopted in the experiments of electron transfer between QDs and NB. After incubation for 10.0 min, a certain concentration of DNA was added into above system and the influence of reaction time on the fluorescence intensity of was also studied. The corresponding result demonstrated that the turn-on sensing platform was adopted to detect DNA after another 10 min (see Figure 7C).

(4) Effect of ionic strength: The influences of ionic strength on the fluorescence intensity of the sensing ensemble were investigated by adding NaCl solution (as shown in Figure 7D). A certain amount of NaCl could not only stabilize the double helix structure of DNA, but also decrease the disturbance of nonspecific substances to ensure the good selectivity of the detection system. The results showed that when the concentration of NaCl was below $0.013 \text{ mol}\cdot\text{L}^{-1}$, the fluorescence intensities remained constant. If the concentration of NaCl was too high, the quenching efficiency of NB-induced the fluorescence of GSH-capped CdTe QDs was decreased, presumably due to the formation of a multilayer ion barrier separating GSH-capped CdTe QDs and NB¹⁸. So, after some systematic studies, $0.013 \text{ mol}\cdot\text{L}^{-1}$ NaCl should be added into the sensing ensemble to establish a double ion layer in the space between GSH-capped CdTe QDs and NB.

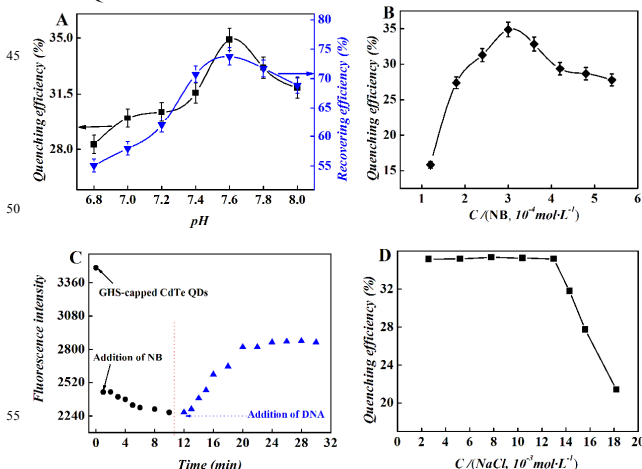


Figure 7 (A) Effect of pH on the fluorescence quenching efficiency (black curve) of GSH-capped CdTe QDs ($3.0\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$) by NB ($6.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$), and subsequent the fluorescence recovering efficiency (blue, curve) by DNA ($20.0 \mu\text{g}\cdot\text{mL}^{-1}$) in $0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl buffer; (B) effect of the concentration of GSH-capped CdTe QDs on the fluorescence quenching efficiency of the reaction system in $0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl buffer at pH=7.6 (NB, $6.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$); (C) effect of reaction time on the fluorescence intensity of the solution system in $0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl buffer at pH=7.6 (GSH-capped CdTe QDs, $3.0\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; NB, $6.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$; DNA, $20.0 \mu\text{g}\cdot\text{mL}^{-1}$); (D) effect of ionic strength on the fluorescence quenching efficiency of the reaction solution in $0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl buffer at pH=7.6 (GSH-capped CdTe QDs, $3.0\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; NB, $6.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$).

DNA determination with the assembling biosensor

According to primary analysis above, NB-induced fluorescence quenching of GSH-capped CdTe QDs was attributed to a new complex formation of NB with GSH-capped CdTe QDs through electrostatic attraction in the excitation wavelength of 350 nm. Consequently, it makes sense for enhancing the fluorescence of the GSH-capped CdTe QDs-NB system in the presence of DNA that is able to bind with NB and then suppress the electron transfer process. The designed protocol was successfully validated in our experiment. As shown in Figure 8, gradually enhanced fluorescence spectra of the assembling biosensor system were observed in the concentration of DNA from 0 to $25.0 \mu\text{g}\cdot\text{mL}^{-1}$. That is, the fluorescence intensity of the assembling biosensor increased rapidly upon addition of DNA in the area. So, the observed NB-induced the fluorescence quenching and subsequent DNA-induced the fluorescence recovery built a solid base for us to develop a QD-based “off-on” fluorescent biosensor for monitoring DNA.

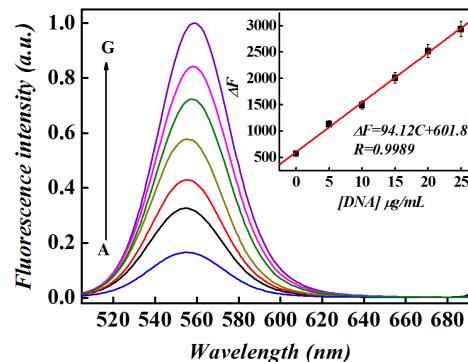


Figure 8 Fluorescence spectra of GSH-capped CdTe QDs with addition of $14.0\times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$ NB recover due to introducing DNA in $0.01 \text{ mol}\cdot\text{L}^{-1}$ Tris-HCl buffer solution at pH=7.6, from curve (A) to curve (F), the concentrations of DNA were 0, 5.0, 10.0, 15.0, 20.0, and $25.0 \mu\text{g}\cdot\text{mL}^{-1}$, respectively; curve (G) is the fluorescence spectrum of GSH-capped CdTe QDs; the inset revealed the relationship of the restored fluorescence intensity of the proposed assembling biosensor with the concentration of DNA. (GSH-capped CdTe QDs, $3.0\times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$).

To evaluate the sensitivity of the proposed “off-on” fluorescent biosensor for the detection of DNA, the fluorescence intensity of the as-prepared assembling biosensor was monitored as a function of the concentration of DNA in the experimental conditions. As demonstrated in the inset of Figure 8, a linear calibration plot of the restored fluorescence intensity ($\Delta F = F - F_0$) against the concentration of DNA was observed in the range of $0.0092\text{--}25.0 \mu\text{g}\cdot\text{mL}^{-1}$ with a correlation coefficient of 0.9989 and a linear regression equation of $\Delta F = 94.12C + 601.87$ (where C is the concentration of DNA in $\mu\text{g}\cdot\text{mL}^{-1}$). A detection limit of 2.78

ng·mL⁻¹ for DNA was determined by using $3\sigma/S$, where σ was the standard deviation of eleven replicate measurements of the fluorescence intensity of the blank samples and S was the slope of the calibration plot. In addition, the sensitivity of this method using the assembling biosensor for DNA detection is not only higher than other fluorescence techniques (FL), but also than those of RRS methods, capillary electrophoresis method (CE) and even higher than that of flow injection chemiluminescence (CL) technique (see Table 2). Thus, it is quite obvious that this assembling biosensor had a nice sensitivity for detecting DNA in aqueous solution.

Table 2 Comparison of the sensitivity of this proposed assembling biosensor with those of other methods for the determination of DNA

Methods	Analytical reagents or detectors	Linear ranges ($\mu\text{g}\cdot\text{mL}^{-1}$)	Detection limits ($\mu\text{g}\cdot\text{mL}^{-1}$)	Ref.
FL	TGA-CdTe/CdS QDs-daunorubicin system	1.38-28.0	0.41	7
FL	Sm ³⁺ -modulated GSH-capped CdTe QDs	0.012-14.0	0.00361	23
FL	Cysteine-capped ZnS nanoparticles	0.1-0.6	0.0246	24
FL	9-Anthracenecarboxylic acid-CTMAB	0.08-1.0	0.019	25
FL	GSH-CdTe QDs-praseodymium(III)-rutin complex system	0.0874-20.0	0.0262	26
RRS	polymyxin B	0.029-3.6	0.009	4
RRS	BleomycinA ₅	0.030-18.60	0.0092	27
RRS	chlorpromazine hydrochloride	0-6.0	0.0116	28
RRS	Glyp-functionalized-CdTe/CdS QDs carbon ionic liquid electrode	0.482-90.0	0.146	29
CE	Ce(IV)-Na ₂ SO ₃ -Tb(III)-fluoroquinolone antibiotic system	50-600.0	17.0	3
CL	The proposed assembling biosensor of GSH-capped CdTe QDs with NB	0.0092-25.0	0.00278	This work

To explore the interaction mode of DNA with this proposed assembling biosensor, the influences of DNA on the fluorescence emission of GSH-capped CdTe QDs were investigated in the absence of NB (as shown in Figure 9). The corresponding result revealed that the fluorescence emission of GSH-capped CdTe QDs was not influenced by the addition of DNA in the concentration of 25.0 $\mu\text{g}\cdot\text{mL}^{-1}$. Hence, DNA had no obvious influence on the fluorescence of GSH-capped CdTe QDs, and the fluorescence intensity enhancement caused by the addition of DNA came from the interaction of DNA with NB. To further prove this hypothesis, RRS spectra of DNA-GSH-capped CdTe QDs-NB system were measured in 0.01 mol·L⁻¹ Tris-HCl buffer solution at pH=7.6. As illustrated in Figure 10, the curve (A), (B) and (C)

were the RRS spectra of GSH-capped CdTe QDs, NB, and GSH-capped CdTe QDs-NB complex system, respectively. The RRS intensities of GSH-capped CdTe QDs and NB are very weak. Whereas, the RRS intensity of GSH-capped CdTe QDs is enhanced in the presence of NB under the experimental conditions. The introduction of DNA apparently decreased the RRS intensity of GSH-capped CdTe QDs-NB system (curve D), which indicated that the complex of GSH-capped CdTe QDs-NB-DNA was not formed. Meanwhile, it was good evidence that the interaction between DNA and NB was not electrostatic attraction or groove binding⁷. Therefore, we speculated that the NB disintegrated from the surface of GSH-capped CdTe QDs and NB embedded into DNA double helix structure³⁰.

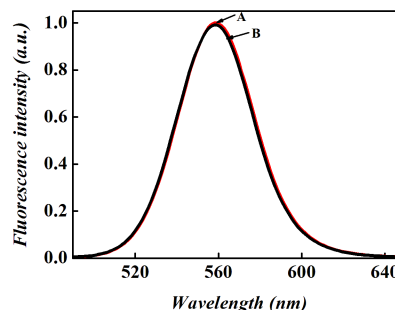


Figure 9 The effect of DNA on the fluorescence intensity of GSH-capped CdTe QDs in 0.01 mol·L⁻¹ Tris-HCl buffer solution at pH=7.6; A (red curve) GSH-capped CdTe QDs only; B (black curve) GSH-capped CdTe QDs in the presence of DNA (GSH-capped CdTe QDs, 3.0×10^{-4} mol·L⁻¹; DNA, 25.0 $\mu\text{g}\cdot\text{mL}^{-1}$).

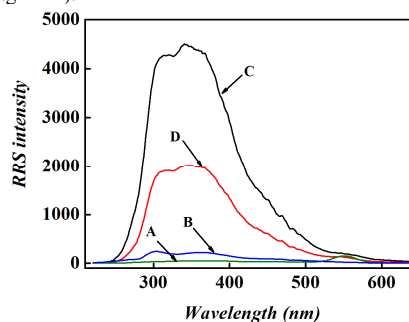
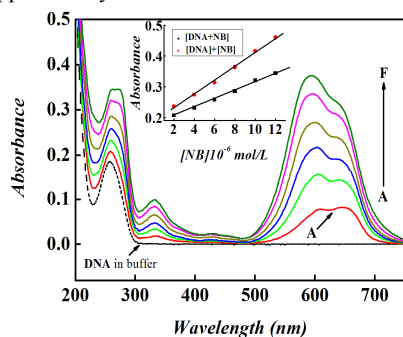


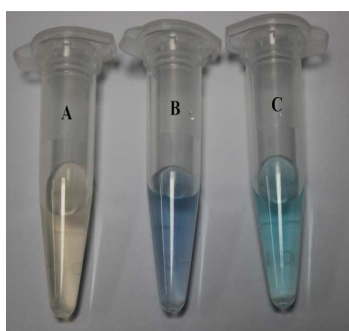
Figure 10 RRS spectra of (A) GSH-capped CdTe QDs; (B) NB; (C) GSH-capped CdTe QDs-NB complex; (D) GSH-capped CdTe QDs-NB-DNA system. (GSH-capped CdTe QDs, 3.0×10^{-4} mol·L⁻¹; NB, 14.0×10^{-6} mol·L⁻¹; DNA, 10.0 $\mu\text{g}\cdot\text{mL}^{-1}$; Tris-HCl, 0.01 mol·L⁻¹, pH=7.6)

Absorption spectroscopy is an effective method to examine the binding mode of DNA with micromolecules. Because of compound binding to DNA, the absorbance spectrum shows hypochromism and hyperchromism. In general, the hyperchromism and hypochromism were regarded as spectral features for DNA double-helix structural change when DNA reacted with other molecules. The hyperchromism means the breakage of the secondary structure of DNA; the hypochromism originates from stabilization of the DNA duplex by either the intercalation binding mode or the electrostatic effect of small molecules³¹. Thus, in order to provide evidence for the possibility of binding of NB with the DNA, the UV-vis absorption spectra of NB-DNA system in 0.01 mol·L⁻¹ Tris-HCl buffer solution at pH=7.6 were investigated as well. As demonstrated in Figure 11A, the characteristic absorption peak of free DNA was at 260 nm, and the absorption increased after the addition of different concentrations of NB. The inset in Figure

10A shows that the absorption value of simple adding free DNA and free NB was greater than the absorption value of DNA-NB complex, which meant a hypochromic effect existed between DNA and NB. It was also observed that the addition of NB to the DNA solution induced the characteristic absorption peak of DNA at 260 nm had a red-shift behavior. In addition, it is very interesting that there is a color change for GSH-capped CdTe QDs-NB-DNA system (see Figure 11B). With the introduction of NB, the color of GSH-capped CdTe QDs changed gradually, initially from (sample A) salmon pink to (sample B) dark blue, and finally to (sample C) sky-blue with the addition of DNA due to the strongly interaction of DNA with NB. This phenomenon further verified the hypochromic effect existed between DNA and NB as well. Since the hypochromism and red-shift behavior were decisive characteristics of intercalative binding, the binding mode of NB with DNA could be unambiguously established to be intercalation³². Above research results indicated that the addition of DNA to the assembling biosensor of GSH-capped CdTe QDs with NB system response induced NB to be dissociated from the surface of GSH-capped CdTe QDs, and then NB embedded into DNA double helix structure to form more stable complex with DNA through intercalation. Hence, the fluorescence intensity of the proposed assembling biosensor could be restored because the electron transfer process between GSH-capped CdTe QDs and NB was suppressed by the addition of DNA.



(A)



(B)

Figure 11 (A) UV-vis absorption spectra of DNA with various concentrations of NB; Inset: comparison of absorption at 260 nm between the DNA-NB complex and the sum values of circular DNA and NB. *c* (DNA)=10 $\mu\text{g}\cdot\text{mL}^{-1}$; *c* (NB)/(10^{-6} mol·L⁻¹), A-F from 2.0 to 12.0 at increments of 2.0. (B) Photographs of the GSH-capped CdTe QDs-NB-DNA system. Sample A: GSH-capped CdTe QDs; Sample B: GSH-capped CdTe QDs-NB complex system; Sample C: GSH-capped CdTe QDs-NB-DNA system; (GSH-capped CdTe QDs, 3.0×10^{-4} mol·L⁻¹; NB, 14.0×10^{-6} mol·L⁻¹; DNA, 10.0 $\mu\text{g}\cdot\text{mL}^{-1}$; Tris-HCl, 0.01 mol·L⁻¹, pH=7.6).

Selectivity and regenerability of the proposed assembling sensor for DNA

To evaluate the selectivity of the proposed assembling fluorescent biosensor for DNA, the influences of some biological species such as metal ions, amino acids, proteins and glucose were examined in 0.01 mol·L⁻¹ Tris-HCl buffer solution at pH=7.6. To the above constructed sensor, the inspected species were added individually, the fluorescence intensities of which were compared to that of the biosensor (denoted as blank). The corresponding results were listed in Figure 12. It was obvious that only DNA enabled the fluorescence of this proposed sensor to be turn-on, indicating a pronounced selectivity of the proposed assembling fluorescent biosensor for DNA.

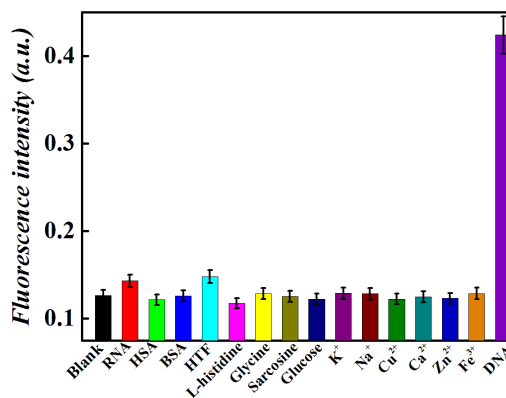


Figure 12 The fluorescence response of this proposed sensor for DNA in the presence of different substances. Conditions: GSH-capped CdTe QDs, 3.0×10^{-4} mol·L⁻¹; NB, 14.0×10^{-6} mol·L⁻¹; DNA, 10.0 $\mu\text{g}\cdot\text{mL}^{-1}$; glucose, 50.0 $\mu\text{g}\cdot\text{mL}^{-1}$; metal ions: K⁺ (1.0×10^{-3} mol·L⁻¹), Na⁺ (1.0×10^{-3} mol·L⁻¹), Cu²⁺ (1.0×10^{-5} mol·L⁻¹), Ca²⁺ (1.0×10^{-5} mol·L⁻¹), Zn²⁺ (1.0×10^{-5} mol·L⁻¹), Fe³⁺ (1.0×10^{-5} mol·L⁻¹); the concentrations of RNA, BSA, HSA and holo-transferrin (HTF) are both 20.0 $\mu\text{g}\cdot\text{mL}^{-1}$; the concentrations of L-histidine, Glycine, and Sarcosine are both 40.0 $\mu\text{g}\cdot\text{mL}^{-1}$.

Although many assays for DNA detection have achieved impressive results, these methods are generally unreusable, and thus, development of a generally regenerated sensing platform for rapid and sensitive detection of DNA remains a compelling goal. As demonstrated in Figure 13A, compared with the initial fluorescence intensity of QDs (curve A), the fluorescence intensity of QDs could be quenched by NB to form an assembling sensor and the quenching efficient reached to 83.77% (curve B). When 25.0 $\mu\text{g}\cdot\text{mL}^{-1}$ DNA was introduced to the sensor, its fluorescence intensity could be enhanced and the degree of recovery was 84.16% (curve C), which referenced to the fluorescence of initially QDs. This assembling fluorescence sensor has been reproducibly detecting DNA three times. The corresponding result showed that the sensor could be renewably used for another once (Figure 13B), which demonstrated that regeneration was another appealing advantage for the “off-on” fluorescent sensor.

Application of the sensor

To confirm the feasibility of the proposed “off-on” fluorescent biosensor for real sample determination, the present biosensor had been applied to determine DNA in fresh serum samples of healthy human using standard addition method. According to the procedure reported in reference³³: A 2.0 mL aliquot of fresh serum sample (healthy human) and 2.0 mL trichloroacetic acid

were mixed thoroughly and centrifuged at 5000 rpm for 5.0 min. the supernatant fluid was diluted to 100.0 mL and 1.0 mL of this solution was pipetted into a 10.0 mL volumetric flask, and then 1.0 mL GSH-capped CdTe QDs, appropriate amounts of NB, 1.0 mL pH=7.6 Tris-HCl buffer solution, and appropriate amounts of DNA were added for determination of DNA concentration. The standard addition method is used to determine five parallel samples for each concentration and the results are listed in Table 3.

It can be seen that fluorescence quenching method has a good repeatability for the determination of DNA concentration in fresh serum samples of healthy human and the relative standard deviation (R.S.D.) are between 2.1% and 4.7%. The method also has a good accuracy and the average recoveries are between 99.58% and 101.70% (Table 3). Therefore, the proposed fluorescent biosensor can be applied to the rapid monitoring of DNA in fresh serum samples of healthy human, which will provide valuable evidence for the practicability of the biosensor in biological samples.

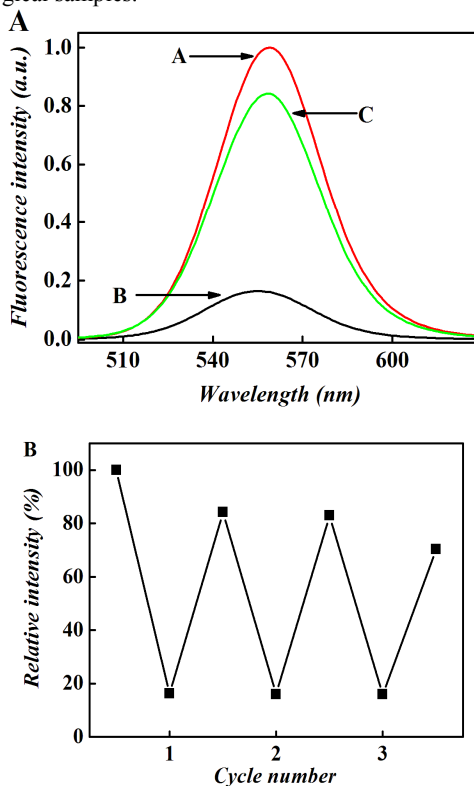


Figure 13 (A) Fluorescence responses of the proposed regenerated sensor. Curve A is the initially fluorescence intensity of QDs ($3.0 \times 10^{-4} \text{ mol} \cdot \text{L}^{-1}$), when NB ($14.0 \times 10^{-6} \text{ mol} \cdot \text{L}^{-1}$) was added, the fluorescence decreased dramatically (curve B); with the addition of DNA ($25.0 \mu\text{g} \cdot \text{mL}^{-1}$), the fluorescence of the above system was restoring (curve C). (B) Reversibility of the sensor over two cycle uses. Relative intensity is calculated with the initial fluorescence intensity value of QDs as 100%.

Table 3 Results for the determination of DNA in fresh human serum samples, $n=5$

Sample	Found ($\mu\text{g} \cdot \text{mL}^{-1}$)	Added ($\mu\text{g} \cdot \text{mL}^{-1}$)	Found ($\mu\text{g} \cdot \text{mL}^{-1}$)	Recovery (n=5, %)	R.S.D. (n=5, %)
1	ND ^d	4.0	3.983	99.58	2.1
2	ND ^d	6.0	6.102	101.70	1.3
3	ND ^d	8.0	7.925	99.06	4.7

^dND: not detected

Conclusions

In summary, we took herring sperm DNA as model DNA and developed a novel assembling fluorescent biosensor for DNA based on electron transfer between GSH-capped CdTe QDs and NB under physiological conditions. With the introduction of NB, the initial fluorescence of GSH-capped CdTe QDs was markedly quenched, which was ascribed to the electrostatic association of NB on the surface of GSH-capped CdTe QDs resulting in the occurrence of an electron transfer process. Upon addition of DNA, the fluorescence recovery behavior of the sensor was observed, which was attributed to DNA induced NB to be dissociated from the surface of GSH-capped CdTe QDs, and then NB embedded into DNA double helix structure to form more stable complex with DNA through intercalation, together with restoring of the fluorescence of GSH-capped CdTe QDs. This present biosensor has demonstrated a regenerability, good selectivity and high sensitivity for DNA in fresh human serum samples, which would be promising for practical application in diverse biological systems.

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Notes and references

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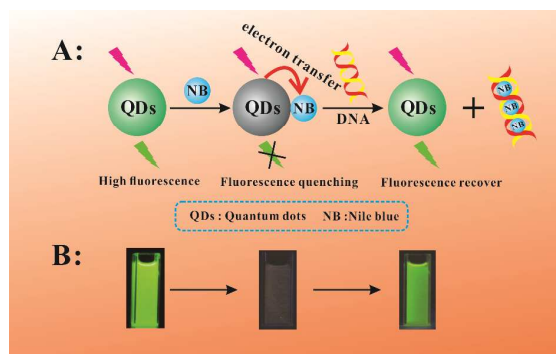
Graphical Abstract

Detection of DNA using an “off-on” switch of regenerable biosensor based on an electron transfer mechanism from glutathione-capped CdTe quantum dots to Nile blue

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A new DNA detection method replying on an “off-on” switch of a regenerated fluorescence biosensor based on an electron transfer mechanism from glutathione (GSH)-capped CdTe quantum dots (QDs) to Nile blue (NB) is proposed.