Trace Hg^{2+} Analysis via Quenching of the Fluorescence of a CdS-Encapsulated DNA Nanocomposite

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Introduction

- Due to its appreciable vapor pressure, mercury remains as a heavy metal whose spectroscopic analysis requires special sample pretreatments or sample introduction systems. For example, for atomic absorption spectrometry and atomic fluorescence spectrometry, cold vapor atomization is required prior to the measurements.

- For ultratrace analysis of Hg^{2+} by inductively coupled plasma mass spectrometry (ICPMS) or inductively coupled plasma atomic emission spectrometry (ICP-AES), the Hg^{2+}-containing aerosol causes serious memory effects, which need to be circumvented with special nebulizers.

- Alternative methods, including the use of metal nanoparticles, semiconductor quantum dots or nanoporous silica have been developed for Hg^{2+} analysis.

In this paper…

- A novel fluorescent CdS-encapsulated DNA nanocomposite was synthesized by alternate adsorption of Cd^{2+} and S^{2-} onto the DNA template confined in an agarose gel.
- The resultant rod-shaped nanocomposite has 40-90nm width and 200-300nm length and fluoresces at 330nm upon exitation at either 228 or 280nm.
- Fluoroscence was found to be quenched by trace amount of Hg^{2+} and a remarkable detection limit of 8.6 nM at 30^0 C was achieved.

Experimental Section

Preparation of the CdS-Encapsulated DNA Nanocomposite.

- DNA stock solution was prepared by dissolving 4.0 mg of calf-thymus DNA in 1.0 mL of phosphate-buffered saline solution (2.0 mM phosphate/10 mM NaCl, pH 7.0)

- A 50 mL aqueous solution containing 2% agarose gel was heated to 65 °C and then cooled to 50 °C. An aliquot of the stock solution containing 2.5 mg of DNA was mixed with the gel solution, and the mixture was aged at 4 °C overnight.

- For the preparation of the CdS/DNA nanocomposite, the gel slab impregnated with DNA was cut into smaller pieces (1-2 mm wide), which were soaked into a 0.5mM $Cd(NO_3)_2$ solution for 48 h to effect a gradual attachment of Cd^{2+} onto the DNA template.

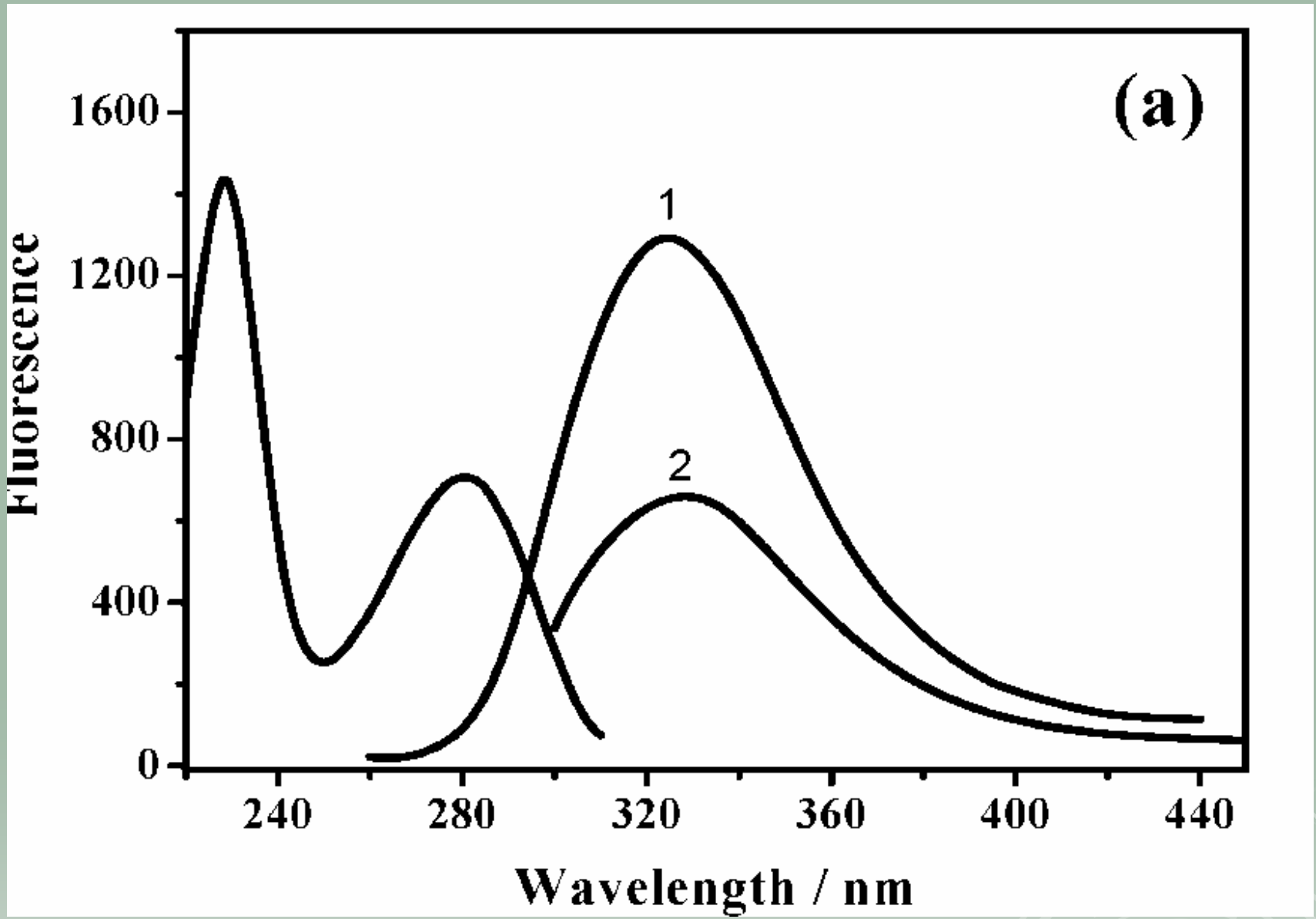
- Thus, the Cd^{2+} infiltration step results in excess Cd^{2+} ions in the matrix, which can interact with the phosphate backbone and heterocycles on the DNA molecule. The above solution was filtered, and the resultant solid was washed with water before being soaked into a 0.5mM Na_2S solution for 48 h

- This step was followed by an extensive wash with water to rid any residual Na_2S solution of the gel. The alternate adsorptions of Cd^{2+} and S^{2-} were repeated for two or three times to form multiple layers of CdS. Finally, upon adding H_2O, the mixture was heated to 65 °C and then filtered to separate the agarose gel from the nanocomposite.

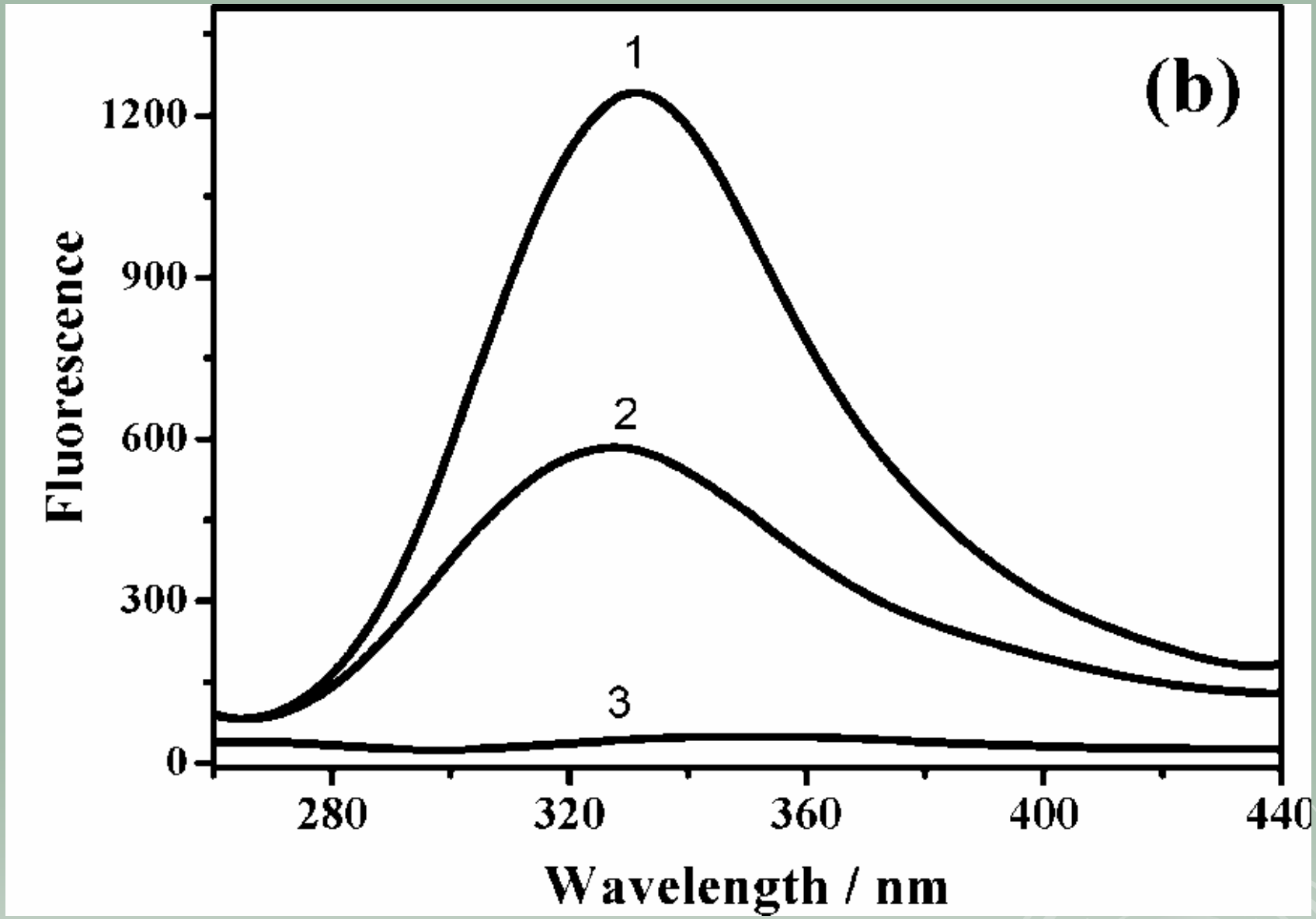
Assay of Hg^{2+} in a Water Sample.

- A wastewater sample, collected from sewerage, was filtrated to remove the suspended solids. The filtrate (200mL) was then condensed to 50mL on a hotplate.

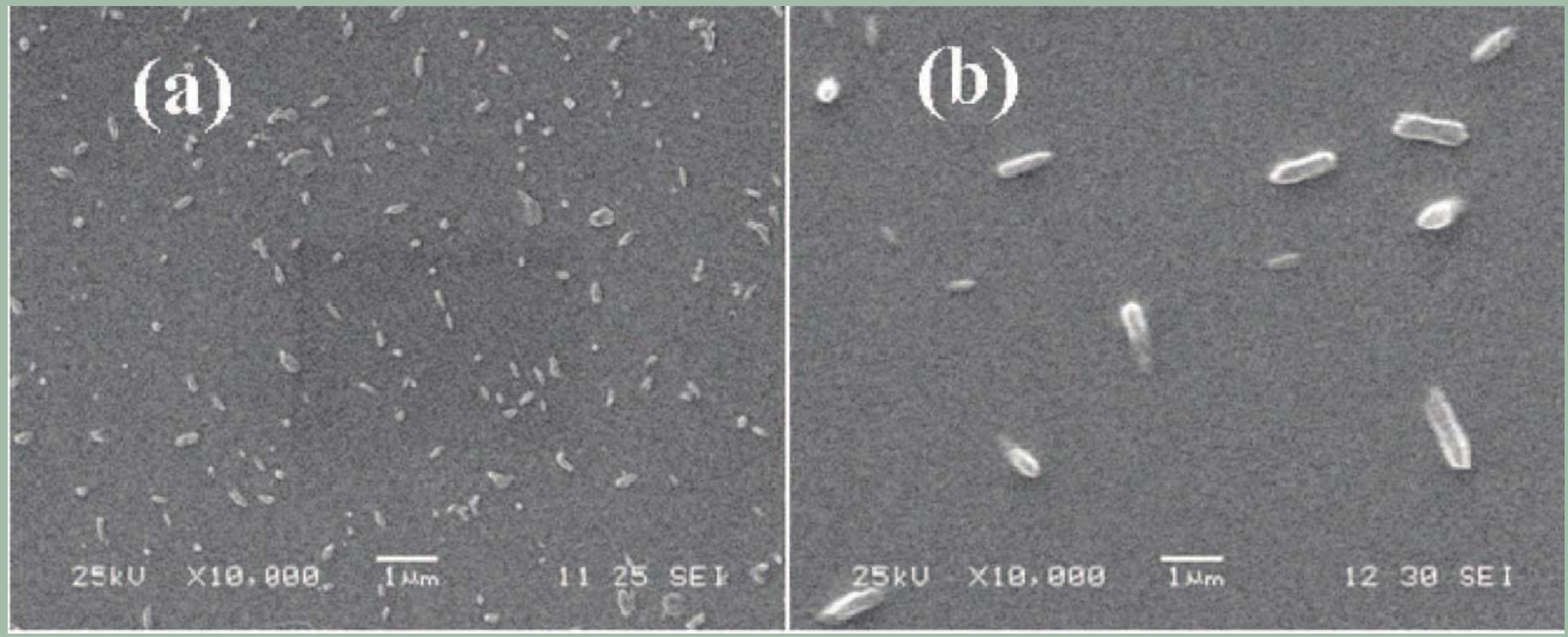
- For Hg^{2+} determination, 150μL of the nanocomposite solution (58μg/mL), 100μL of Britton-Robinson buffer, and an appropriate amount of a Hg^{2+} standard solution or the water sample were mixed thoroughly and then diluted to 1.0mL. The final pH of the solution was maintained at 3.8. Fluorescence measurements were performed after equilibrating the solution for 5 min.



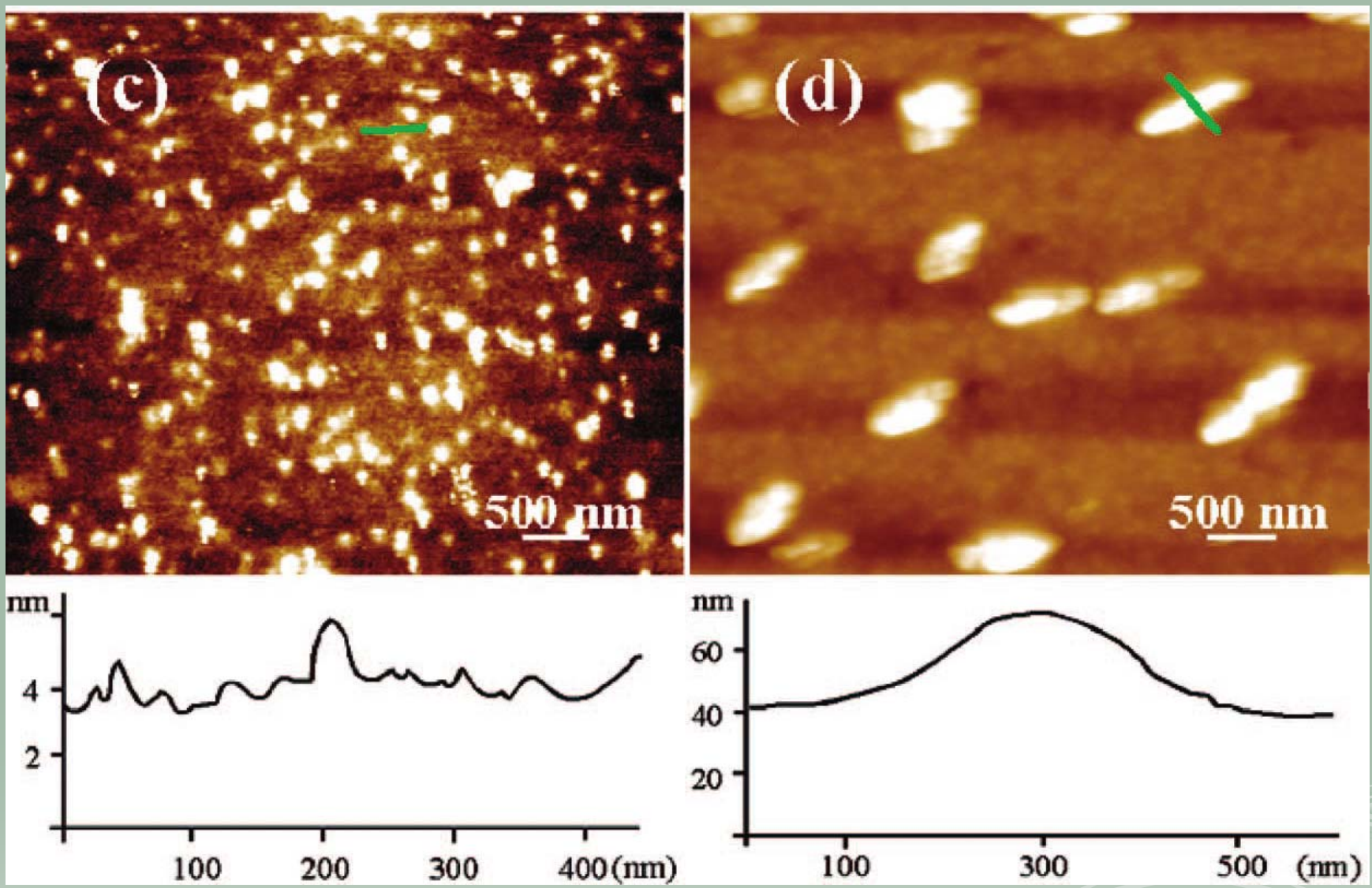
Excitation spectrum (left curve) of 8.7 *μ*g/mL CdS/DNA nanocomposite solution measured with 330 nm as the emission wavelength and the emission spectra (right curves) collected with the excitation wavelengths at 228 nm (curve 1) and 280 nm (curve 2), respectively.



The fluorescence spectra of the CdS/DNA nanocomposite in the absence (curve 1) and presence of 20 μM (curve 2) and 200 μM Hg^{2+} (curve 3). The excitation wavelength was set at 228 nm.



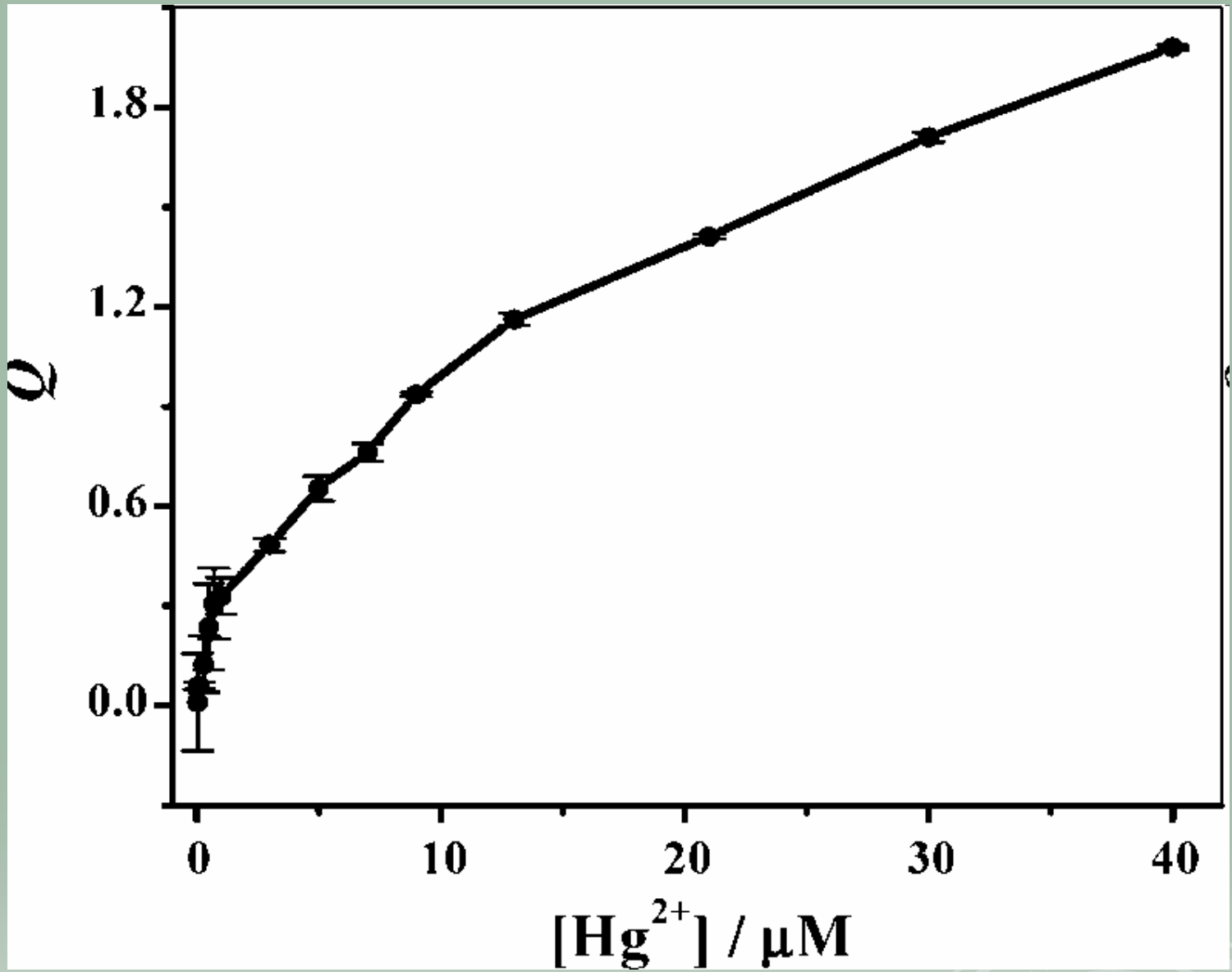
Scanning electron micrographs (a and b) of CdS/DNA nanocomposite cast onto a silicon wafer(a) and the same material that had been exposed to a 200 μM Hg^{2+} solution (b)



AFM images (c and d) of CdS/DNA nanocomposite cast onto a silicon wafer (c) and the same material that had been exposed to a 200 μM Hg^{2+} solution(d). The cross-sectional contours of representative nanocomposites in panels c and d are also shown

$$\frac{F_0 - F}{F} = Q = K_{sv}c$$

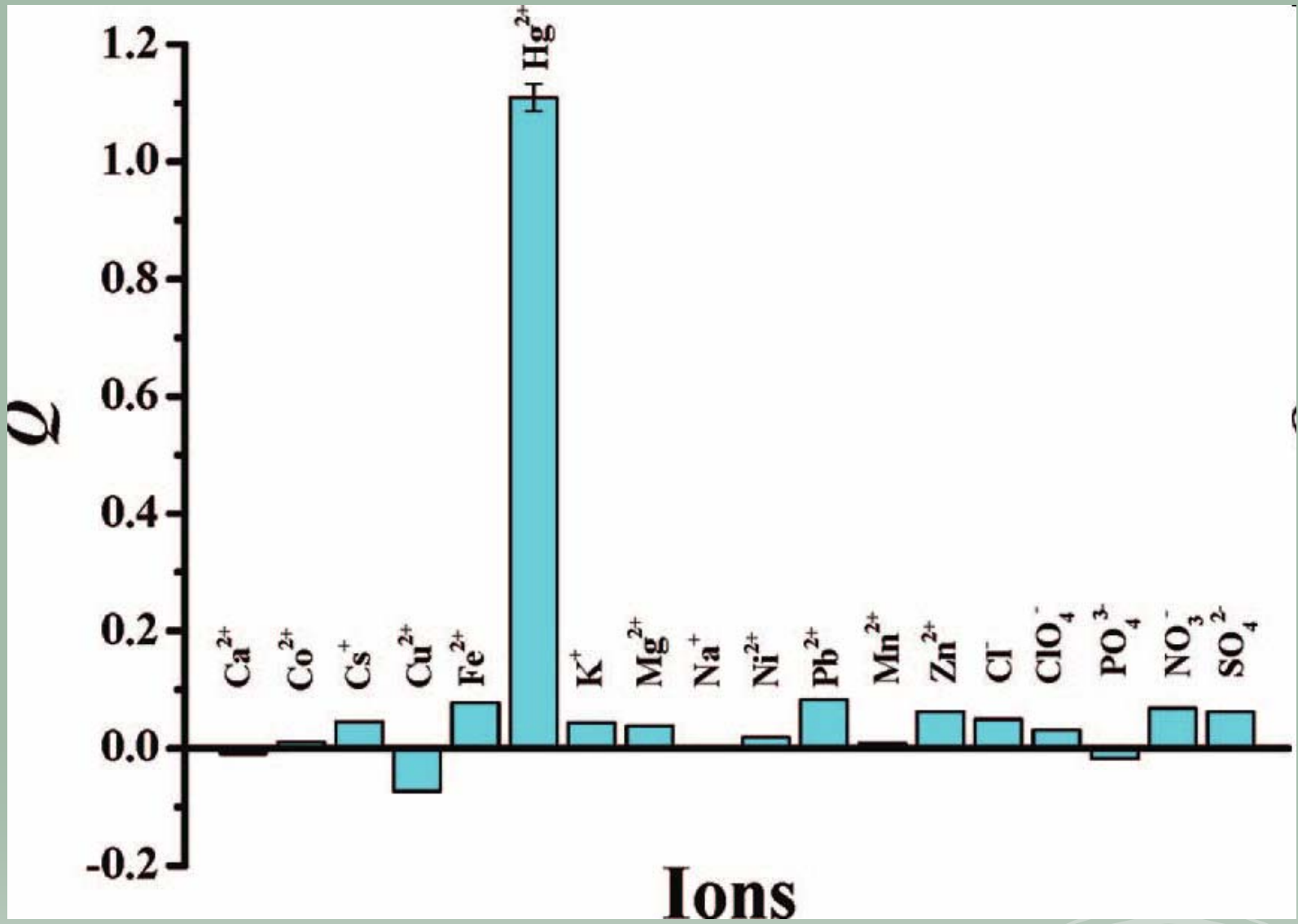
- The quenching of the fluorescent probes follows the **Stern-Volmer equation**, via either a dynamic or a static mechanism: where F_0 and F denote the fluorescence intensities in the absence and presence of an analyte, respectively. K_{SV} is the Stern-Volmer quenching constant and c is the analyte concentration.



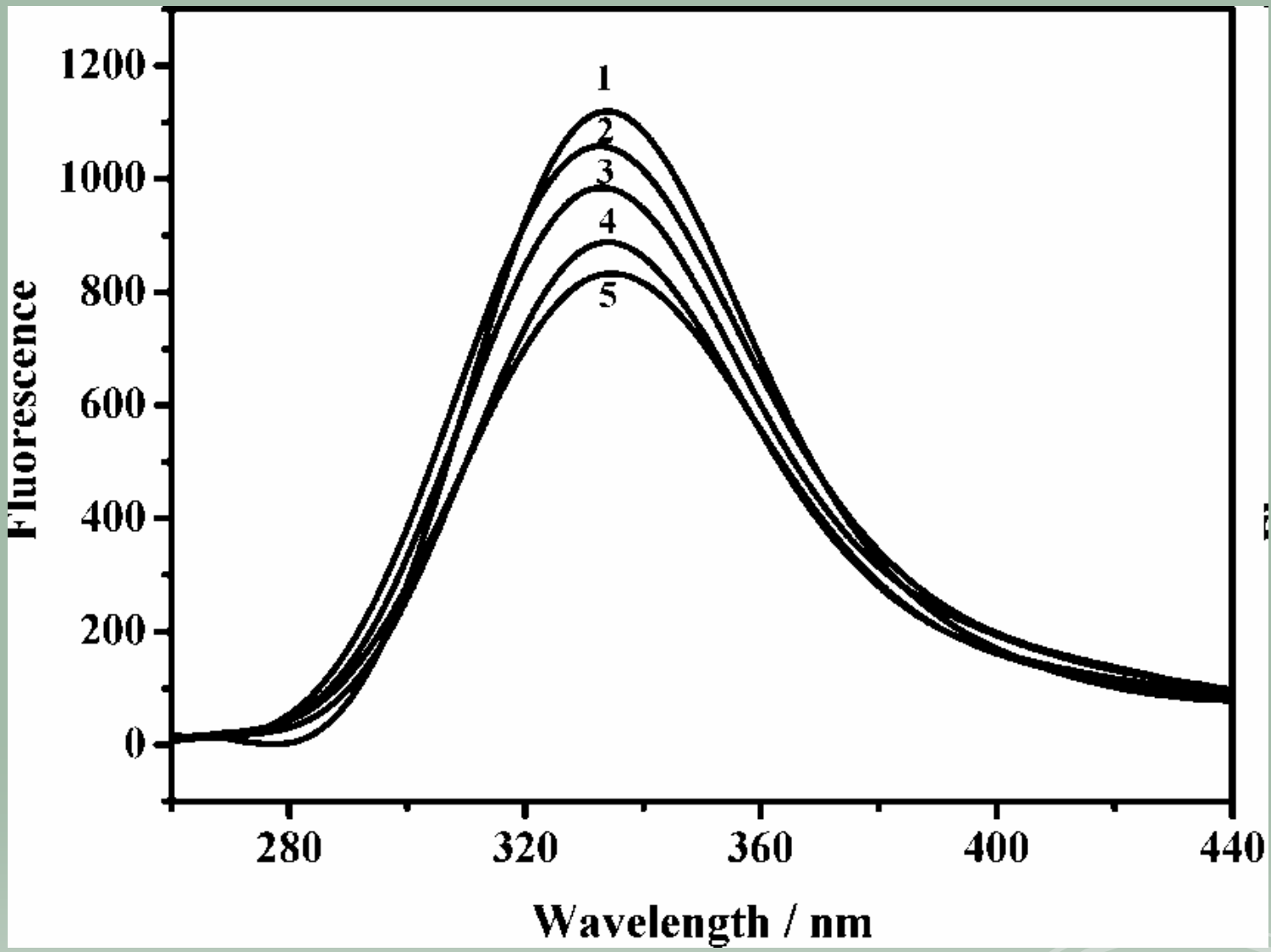
Plot of the *Q* value against Hg^{2+} concentration. Concentrations of Hg^{2+} used were 0.04, 0.1, 0.3, 0.5, 0.7, 1.0, 3.0, 5.0, 7.0, 9.0, 13, 21, 30, and 40 *μ*M. Each point was averaged from at least three replicates, and the relative standard deviations (RSDs), shown as the error bars, range from 0.7% to 14.6%. The solution temperature was maintained at 30 °C.

Table 1. Results for Hg^{2+} Detection at Different Temperatures

T (°C)	linear range in the lower region (μM)	linear regression equation	correlation coefficient (r)	detection limit (nM)
30	0.04–0.7	$Q = 0.444c + 0.002$	0.995	8.6
40	0.02–0.1	$Q = 2.61c + 0.0003$	0.995	6.7
50	0.01–0.11	$Q = 2.74c + 0.026$	0.970	4.3



Effect of different metal ions and anions on the *Q* value.The concentrations of the metal ions used were 20 μM. The concentration of NO^{3-} is 40 μM, and those of other anions are all 200 μM. The absolute error for Hg^{2+} is shown as the error bar and the relative standard deviation (RSD) for Hg^{2+} is 2.1%.



Fluorescence spectra of 8.7 μg/mL CdS/DNA nanocomposite in pure water (curve 1) and the water sample (curve 2). Curves 3-5 correspond to the spectra collected from the water sample that was spiked with 0.2, 0.4, and 0.6 μM standard Hg^{2+} solution respectively.

Conclusions

- A highly sensitive and selective Hg^{2+} fluorescent sensor based on a novel CdS-encapsulated DNA nanocomposite has been developed.
- The nanocomposite adopts a rod-shaped structure and can be dispersed uniformly in solution.
- When excited at either 228 or 280 nm, the nanocomposite yields a distinct emission at 330 nm, which can be significantly quenched by Hg^{2+} in sample solution.
- This novel material also possesses a high selectivity toward Hg^{2+} analysis, as a number of metal ions and anions were found to either not quench or quench the fluorescence at an insignificant level.
- The feasibility of the method for the analysis of a wastewater sample that was not extensively treated or digested was demonstrated.

Relevance…

The strong tendency of mercuric ions to bond with sulphur is being exploited here.

Nanosysytems having a sulphur containing group and which show good fluorescence can be studied for selective and trace determination of mercuric ions.

Thank you