Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting information

Fluorescence analysis of cobalt(II) in water with β-cyclodextrins modified Mn-doped ZnS quantum dots

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Fig. S1 The locations of ditches and factories (a: local furniture factory, b: local battery factory, c and d: the photo of a, e and f: the photo of b).

The irrigation water around the factories may be affected by some illegal discharge of industrial wastewater. In the Sichuan province of China, it is known that there are still some factories near the farmland (Fig. S1).

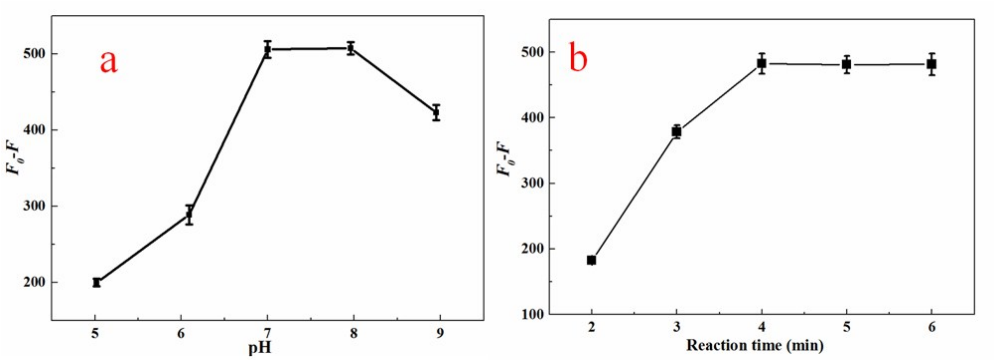

Fig. S2 The results of the optimization for pH and detection time.

The results of the optimization for pH and detection time were shown in Fig. S2. For the optimization for pH, 0.1 mL of 1 mmol/L of the β-CDs@QDs suspension, 0/0.2 mL of 100 μmol/L Co^{2+} solution was added into 1.9/1.7 mL of BR buffer with different pH (5.02, 6.09, 7, 7.96 and 8.95), respectively (the total volume of each sample was 2 mL). From Fig. S2a, it was seen that the relative FL intensity (F_0-F) increased firstly and then decreased with the augmenting of pH, where F_0 was the FL intensity without Co^{2+} (arbitrary unit, a.u.), F was the FL intensity with 10 μmol/L Co^{2+} (a.u.). The relative standard deviation (RSD%) was 1.52-3.77%. The F_0-F of pH at 7 and 8 was almost the same, so 7 was selected as the optimal pH.

Detection time of 2, 3, 4, 5 and 6 min was also studied (Fig. S2b) in this work. 0.1 mL of 1 mmol/L of the β-CDs@QDs suspension was mixed with 0/0.2 mL of 100 μmol/L Co^{2+} solution and BR buffer for different time, of which the total volume was controlled to be 2 mL. The relative FL intensity (F_0-F) was increased from 2-4 min and had little change after 4 min (F_0 was

constant from 2-5 min). The RSD% was 1.67-4.42%. Therefore, the optimal detection time was 4 min.

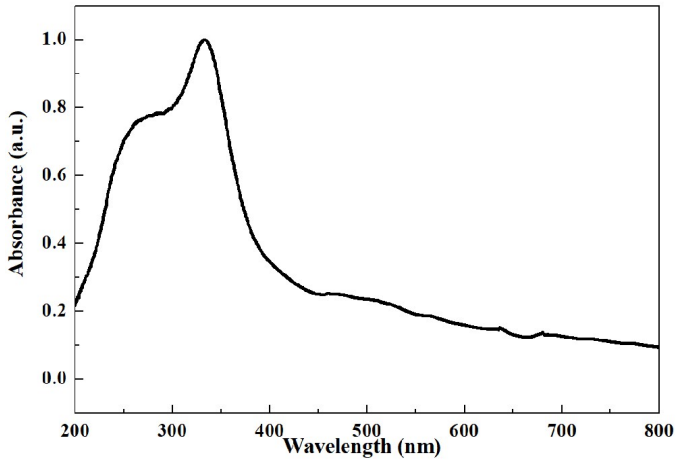

Fig. S3 The UV-vis absorption spectrum of β-CDs@QDs.

Table S1

The comparison of the stability for the modified QDs of this work and the literature.

QDs	time (months)	reference
β-CDs@QDs	1.5	this work
β-CD@ZnO QDs	1	[14]

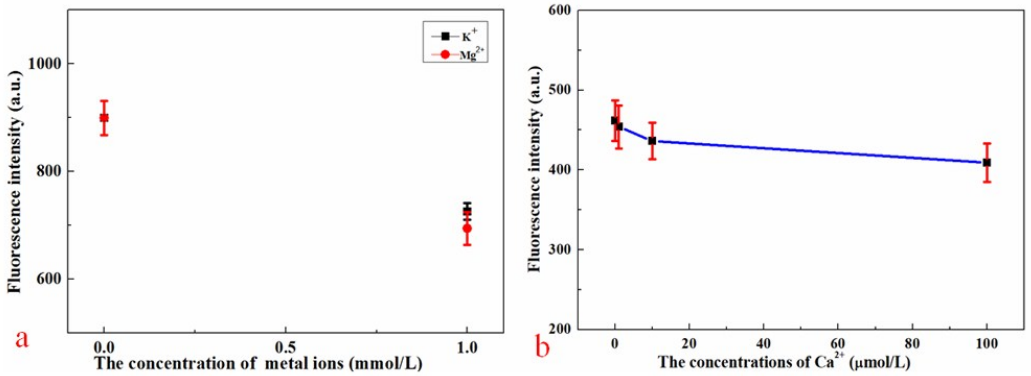

Fig. S4 a: The results for the effect of 1mmol/L K^+ and Mg^{2+} on the FL quenching for Co^{2+} and b: the FL intensities of the modified QDs in the presence of Co^{2+} (10 μmol/L) and Ca^{2+} at different concentrations (0, 1, 10 and 100 μmol/L).

The FL intensities of the modified QDs in the presence of Co^{2+} (10 μmol/L) and Ca^{2+} at different concentrations (0, 1, 10 and 100 μmol/L) were shown in Fig. S4b. The RSD% was 2.13%-6.53%. From Fig. S4b and Fig. 6, the FL quenching of β-CDs@QDs for Co^{2+} was found to be affected by other metal ions. Meanwhile, the influence of metal ion with high concentration was found to be larger than that with low concentration.

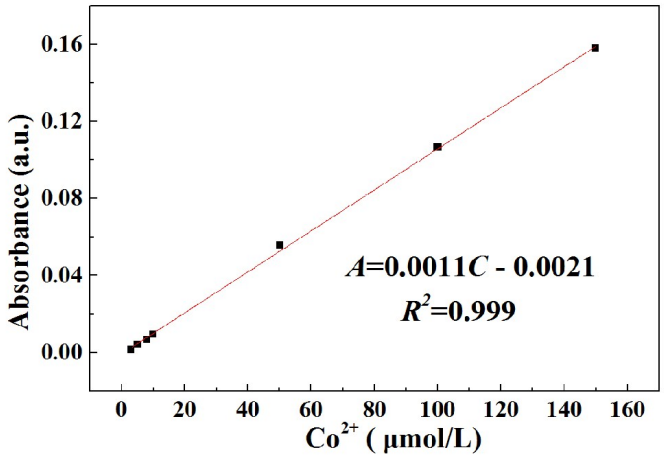

Fig. S5. The standard curve for the absorbance and the concentration of Co^{2+} based on FAAS.

The standard curve for Co^{2+} by FAAS method at the concentration of 3, 5, 8, 10, 50, 100 and 150 μmol/L was revealed in Fig. S5, where *A* was absorbance and *C* was the concentration of Co^{2+} in the formula. The RSD% was 0.10%-3.43%.

Table S2

The interpretations of drilling fluid related to this work.

drilling fluid	description
role	a mixture liquid used in the process of drilling deep wells or boreholes for oil or gas exploration and development, core sampling, and so on
composition	containing various inorganic ions and some polymers
environment hazard	endangering agricultural water after the illegal discharge near the farmland

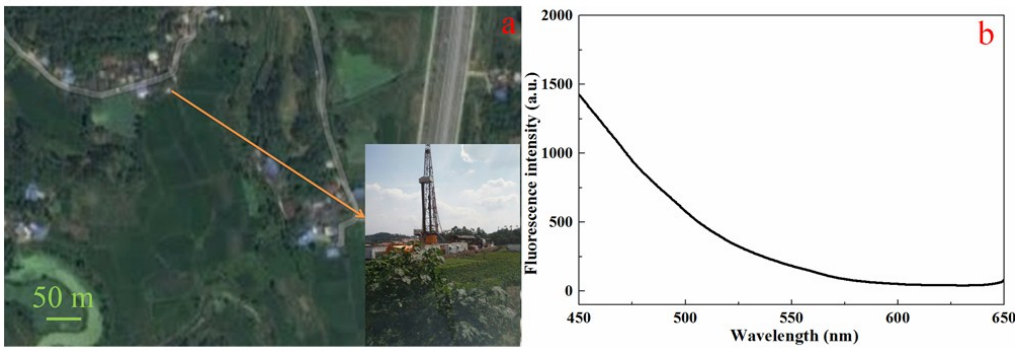

Fig. S6. The approximate location of the well site (a), the photo of the well site (the inset in a) and the FL spectra of the detection of Co^{2+} by the proposed method for the treated wastewater of drilling fluid (b).

Table S3
The concentrations of some metal ions in the wastewater of drilling fluid (obtained from mud engineer).

concentration	mmol/L
K^+	87.23
Ca^{2+}	12.61
Cl^-	135.89
other ions	unknown

References

14 S. Geng, S. M. Lin, Y. Shi, N. B. Li and H. Q. Luo, *Microchim. Acta*, 2017, **184**, 2533-2539.