# Electronic Supplementary Material

# A simple and sensitive flow injection method based on catalytic activity of CdS quantum dots in acidic permanganate chemiluminescence system for determination of formaldehyde in water and wastewater

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## 1. Experimental

## 1.1. Official fluorimetric Method for determination of formaldehyde

The official fluorimetric method is based on the Hantzsch reaction between acetylacetone, ammonia, and formaldehyde to form the dihydropyridine 3,5-diacetyl-1,4-dihydrolutidine (DDL).[1] Quantification can be performed by UV/Vis spectroscopy at 412 nm. The molecule also exhibits fluorescence, thus offering the possibility of selective fluorimetric determination at 510 nm, since other carbonyl compounds do not form strongly fluorescent Hantzsch products.[57] Equal volumes (2 mL) of the standard formaldehyde solutions and a reagent consisting of 2 mol $L^{-1}$ ammonium acetate and 0.02 mol $L^{-1}$ acetylacetone (adjusted to pH 6.0 with acetic acid) are mixed and incubated at 37 °C for 1 h. After cooling to room temperature, intensity was determined at fluorescence excitation and emission wave lengths of 410 and 510 nm, respectively.

The standard curve is linear with formaldehyde from 5 µg $L^{-1}$ to 400 µg $L^{-1}$ and deviates slightly from linearity from 400 µg $L^{-1}$ to 1000 µg $L^{-1}$. Above 1000 µg $L^{-1}$, the formaldehyde can be determined colorimetrically at 412 nm with spectrophotometer.

**Figure captions**

**Figure S1.** Schematic diagram of flow injection CL system; (a): acid solution; (b): sample or standard solution of mixture of HCHO and CdS QDs; (c): $H_2O$ as the carrier; (d): $KMnO_4$ solution; P: peristaltic pump; M: mixing tube; V: injection valve; F: flow cell; W: waste; D: detector (luminometer); R: recorder (personal computer).

**Figure S2.** FT-IR spectra of L-cysteine and L-cysteine capped CdS QDs

**Figure S3.** CL response of $KMnO_4$–CdS QDs in the presence of different concentration of (a): Acetaldehyde (b): Propionaldehyde, (c): Butyraldehyde and (d): Benzaldehyde. The concentrations of $KMnO_4$, HCl, and CdS QDs, were 0.06 mmol $L^{-1}$, 1.0 mol $L^{-1}$, 0.7 mmol $L^{-1}$, respectively.

**Figure S4**. Kinetic curves for (a): $KMnO_4$–CdS QDs (b): $KMnO_4$–CdS QDs–glutaraldehyde, (c): $KMnO_4$–CdS QDs–glyoxal, and (d): $KMnO_4$–CdS–HCHO CL system. The concentrations of $KMnO_4$, HCl, CdS QDs, glutaraldehyde, glyoxal, and HCHO were 0.06 mmol $L^{-1}$, 1.0 mol $L^{-1}$, 0.7 mmol $L^{-1}$, 0.4 mg $L^{-1}$, and 0.4 mg $L^{-1}$, and 6.1 µg $L^{-1}$, respectively.

**Figure S5.** Optimization of the CL reaction conditions: (a) effect of $KMnO_4$ concentration. Conditions: the concentrations HCHO, HCL, and CdS QDs were 1.2 µg $L^{-1}$, 0.5 mol $L^{-1}$, and 0.48 mmol $L^{-1}$, respectively; (b) effect of type and concentration of acidic media. Conditions: the concentrations of $KMnO_4$ was 0.06 mmol $L^{-1}$, other conditions were as in (a), (c) effect of CdS QDs concentration. Conditions: the concentrations of HCl was 1.0 mol $L^{-1}$, other conditions were as in (b).

**Figure S6**. Kinetic curves for (a): $KMnO_4$–CdS QDs (b): $KMnO_4$–CdS QDs–gallic acid, (c): $KMnO_4$–CdS QDs–rutin, (d): $KMnO_4$–CdS–vanillin, and (d): $KMnO_4$–CdS–queretin CL system. The concentrations of $KMnO_4$, HCl, CdS QDs, and phenolic compound (gallic acid, rutin, vanillin, and queretin) were 0.06 mmol $L^{-1}$, 1.0 mol $L^{-1}$, 0.7 mmol $L^{-1}$, 5.0 mg $L^{-1}$, respectively.
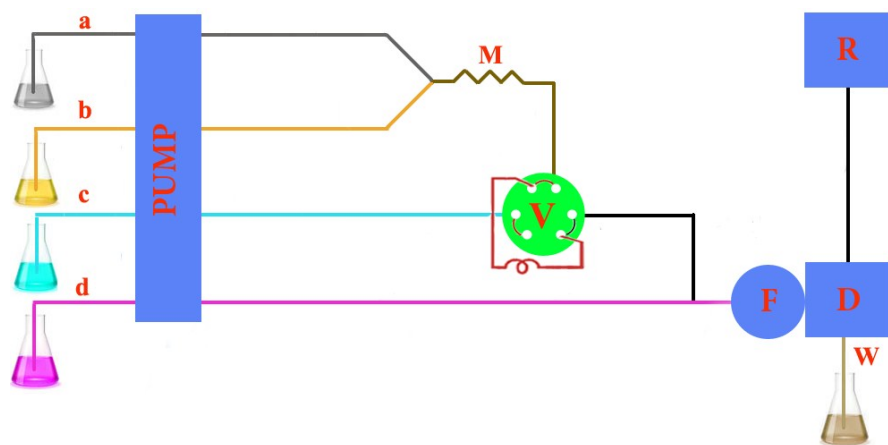
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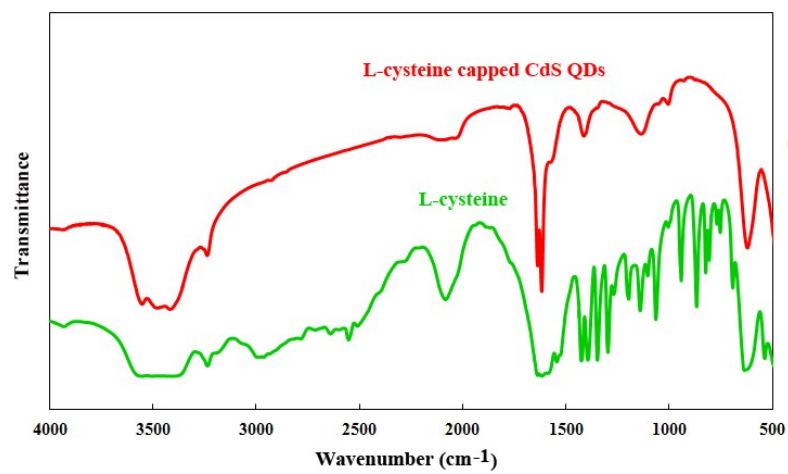
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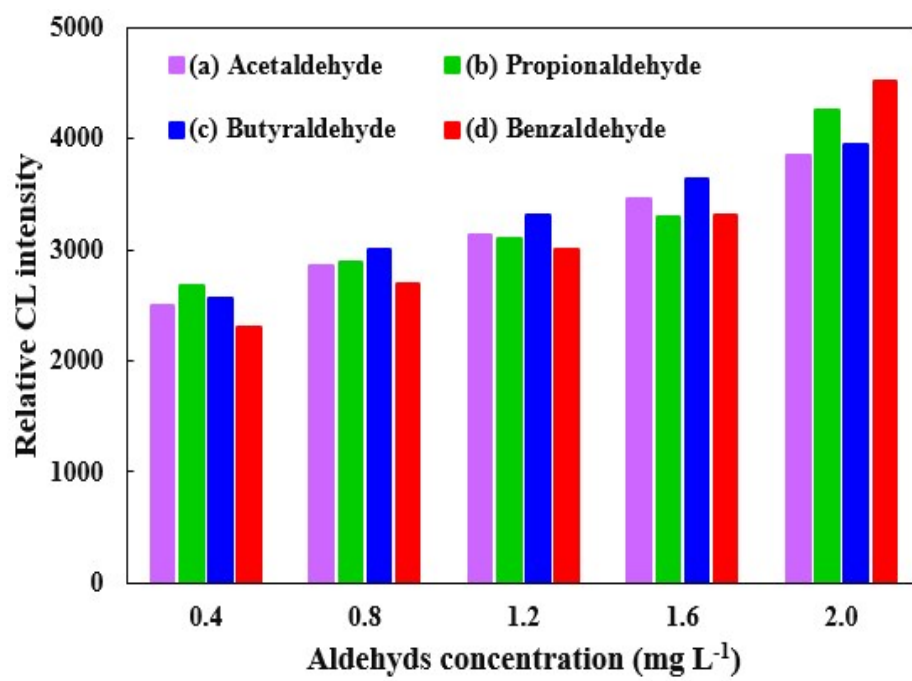
**Figure S3.**

**Figure S4.**

**(a)**

**(b)**

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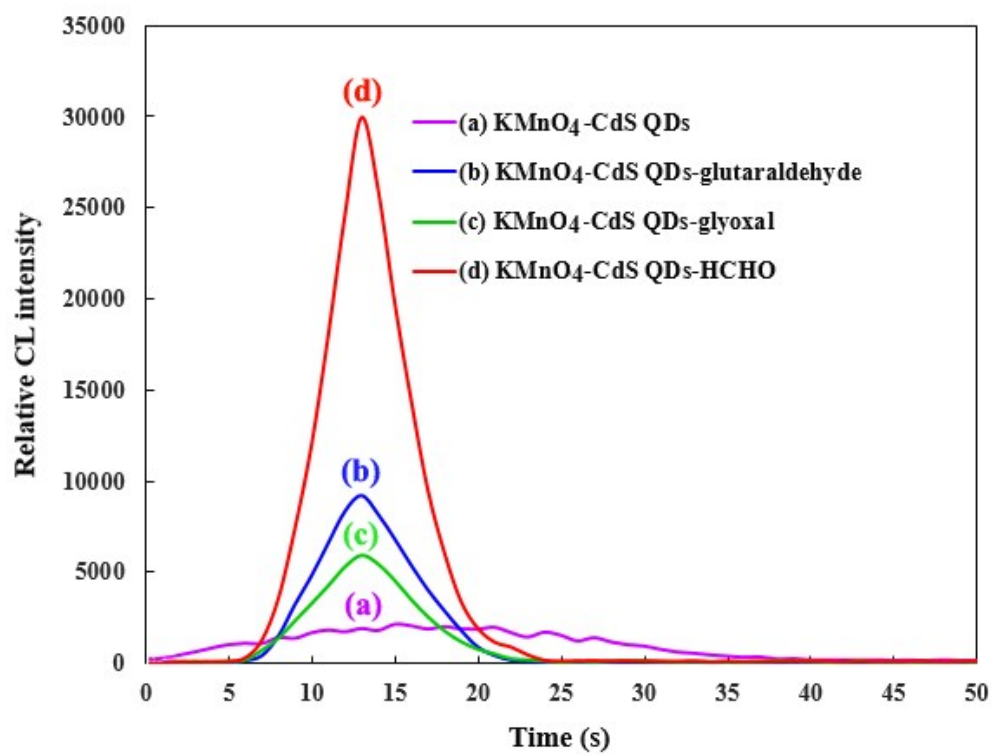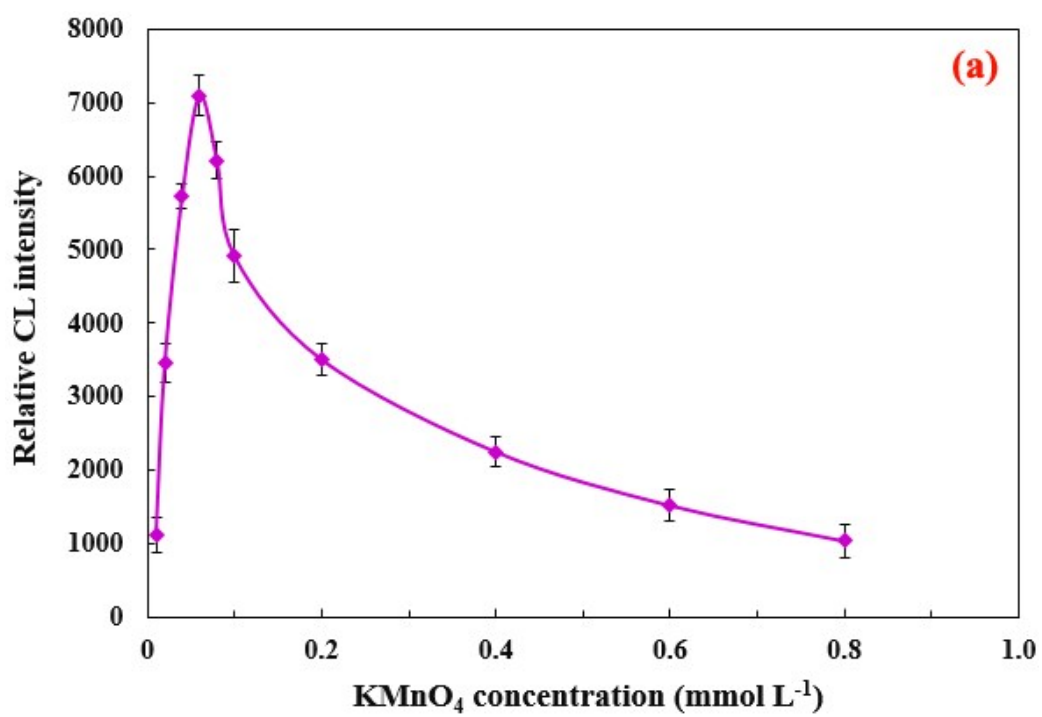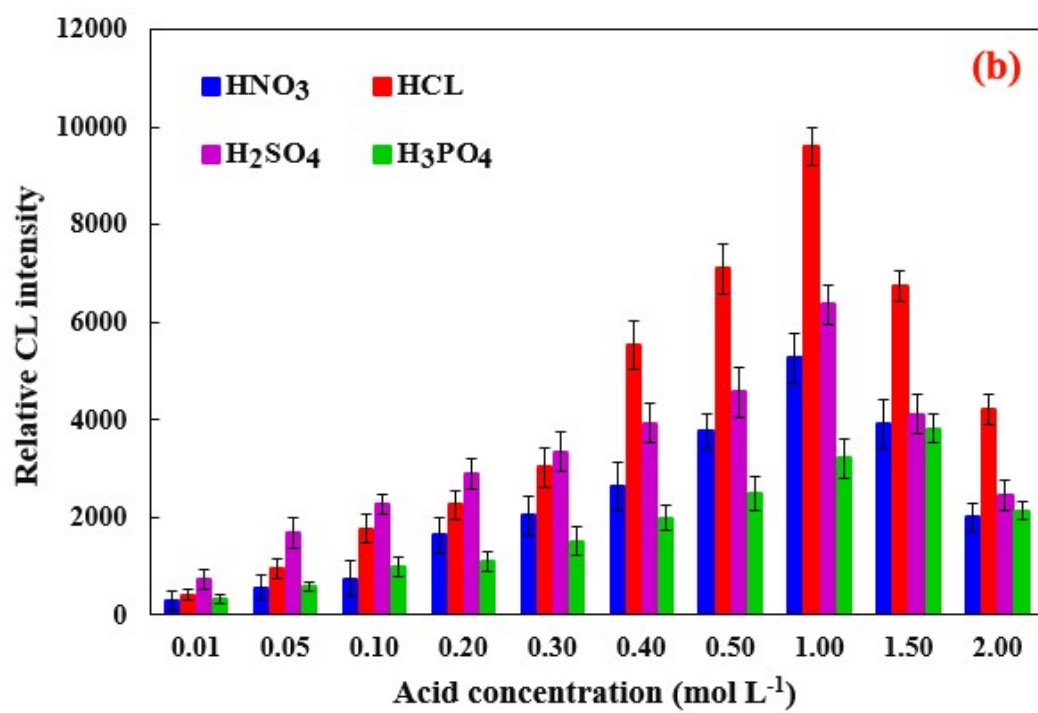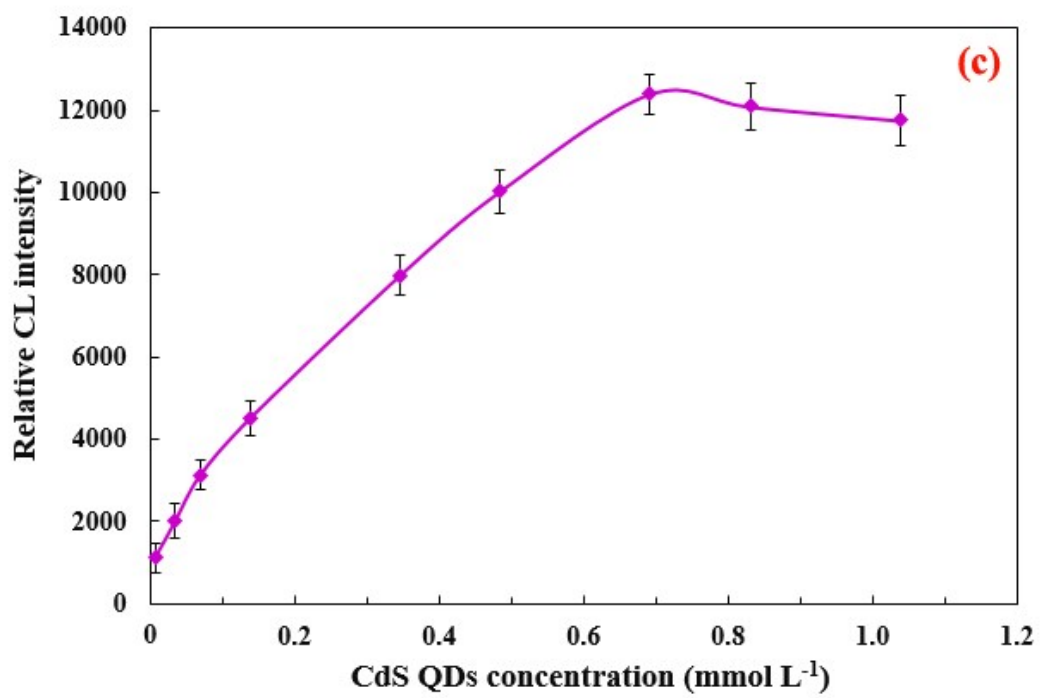
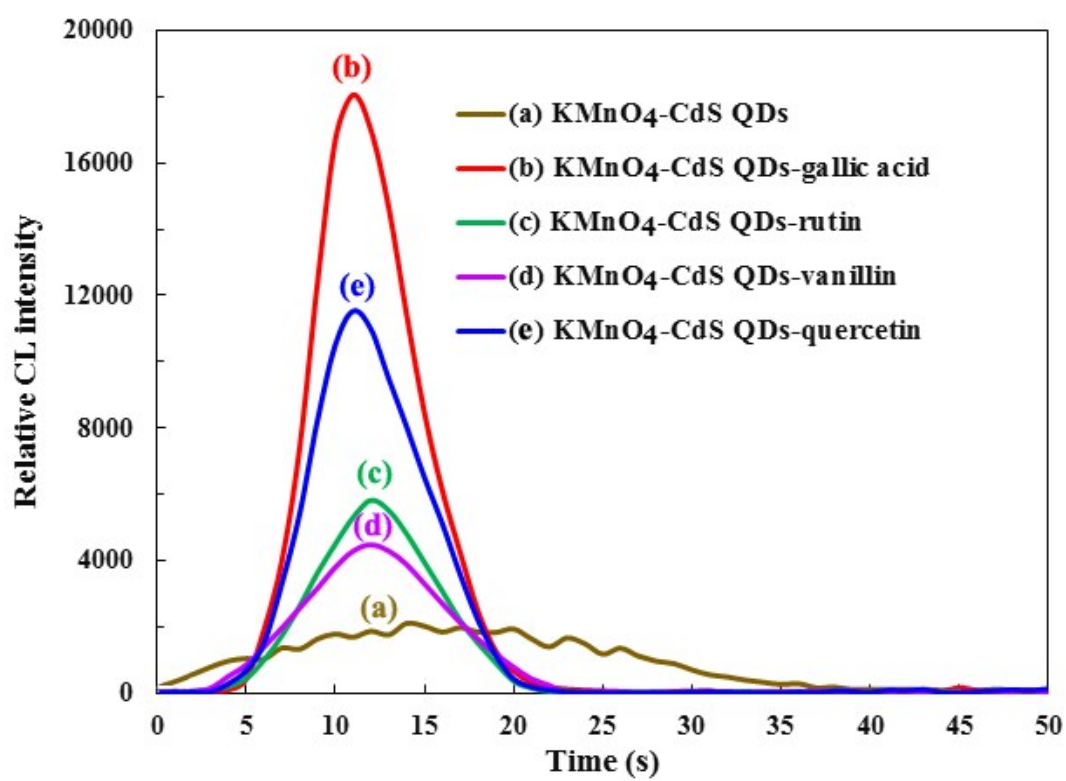**(c)**

**Figure S5.**

**Figure S6.**

# Table

**Table S1.** Tolerable concentration ratios with respect to 5.0 µg L$^{-1}$ of HCHO.

| Species | Tolerable concentration ratio ($10^3$) [$C_{interferent\ (µg/L)}/C_{CHCHO\ (µg/L)}$] |
|---|---|
| Na$^+$, Cl$^-$, K$^+$, SO$_4{}^{2-}$, CH$_3$COO$^-$ | 1100 |
| Br$^-$, CO$_3{}^{2-}$, PO$_4{}^{3-}$, Mg$^{2+}$, Ca$^{2+}$, Tartaric acid, Lactose, Valine | 550 |
| Alanine, Sucrose, Glucose, Starch, NO$_3{}^-$ | 230 |
| Methyl parabene, Propyl parabene | 140 |
| Methanol | 280 |
| Ethanol | 500 |
| Phenol | 150 |
| Vanillin | 85 |
| Queretin | 51 |
| Rutin | 78 |
| Gallic acid | 38 |
| Acetaldehyde, Propionaldehyde, Butyraldehyde, Benzaldehyde | 150 |
| Acetone | 200 |
| Ni$^{2+}$, Pb$^{2+}$, Al$^{3+}$, Zn$^{2+}$ | 50 |
| Fe$^{2+}$, Co$^{2+}$ | 30 |
| Cu$^{2+}$ | 8 |

**References**

1.  S. Belman, The fluorimetric determination of formaldehyde, *Anal. Chim. Acta*, 1963, **29**, 120-126