# Analytical Methods



View Article Online

View Journal | View Issue

# PAPER

() Check for updates

Cite this: Anal. Methods, 2022, 14, 2368

Received 21st February 2022 Accepted 5th May 2022

DOI: 10.1039/d2ay00297c

rsc.li/methods

## Introduction

Mercury ions  $(Hg^{2+})$  are one of the most deadly heavy metal pollutants because they are easily transported from the environment to the food chain, accumulating in the human body and causing major damage to the brain, neurological system, endocrine system, kidneys, and other organs.<sup>1,2</sup> The development of rapid, sensitive and accurate methods for quantitative determination of Hg<sup>2+</sup> is of great significance to environmental protection and human health.<sup>3</sup> At present, there are many methods to detect mercury ions.4-7 However, the development of a highly sensitive and specific mercury ion sensor is still the unremitting pursuit of researchers. Due to the strong affinity between mercury ions and ligands containing sulfur atoms, many compounds have been used as capture probes for mercury ions.<sup>8,9</sup> Therefore, how to make use of the strong coordination between sulfhydryl and mercury ions to selectively detect mercury ions and get rid of the limitations of biosensors is worth the effort.

Electrochemiluminescence (ECL) analysis technology with the advantages of convenience and high sensitivity has a wide

# A novel sensor for visual and selective detection of Hg<sup>2+</sup> based on functionalized doped quantum dots<sup>+</sup>

Zhipeng Wu, <sup>(b)</sup> ‡ Chenglin Dai, ‡ Yiwu Wang, ‡ Lianju Ma, Guangchao Zang, Qian Liu <sup>(b)</sup> and Shu Zhu <sup>(b)</sup> \*

In this paper, a novel analytical platform for the visual, sensitive and reliable analysis of mercury ions (Hg<sup>2+</sup>) is fabricated based on functionalized doped quantum dots. We synthesized a new specific nano-material, zinc dithiothreitol combined with graphene quantum dots (ZnNCs–NGQDs), by a simple and convenient method which, as an efficient luminophore, was then applied to construct an electrochemiluminescence (ECL) system for the first time. Under optimized conditions, the ECL sensor showed an excellent response for Hg<sup>2+</sup> in the linear range of 1.0 mM to 10 pM, with a low detection limit of 3 pM. Moreover, the proposed method demonstrated satisfactory selectivity, stability and acceptable reproducibility for the detection of Hg<sup>2+</sup>. The recovery of tap water and lake water samples ranged from 96% to 105%, indicating the potential applicability of the proposed method for monitoring environmental water samples. Meanwhile, visual attempts for mercury ion detection by using doped quantum dots have also obtained satisfactory results. Importantly, our research revealed a viable method for improving the sensitivity and convenience of target studies in sensing fields derived from functional material design.

> range of applications in the fields of biomedical analysis, clinical laboratories and environmental detection.<sup>10,11</sup> Graphene quantum dots (GQDs) in the ECL system are a class of lowdimensional semiconductor nanomaterials with obvious quantum effects.<sup>12,13</sup> The photoelectric performance of GQDs is determined by the interplay of the structure and interface, which can be improved through size changes, surface functional groups, and heteroatoms.<sup>14,15</sup> It has been discovered that graphene quantum dots doped with nitrogen, sulfur, and other heteroatoms are not only simple to make but significantly boost ECL performance.<sup>16,17</sup>

> Metal nanomaterials, especially zinc (Zn) nanomaterials with low toxicity, have a lot of unsaturated coordination active atoms on their surface, which can bind to molecules containing the sulfhydryl group and amino group.18,19 There are results that show that the optical properties of organic luminescent materials can be improved effectively by introducing metal zinc into organic luminescent materials to form zinc complexes.<sup>20</sup> At the same time, it is surprising that the introduction of metal-zinc compounds or metal-zinc complexes can improve the ECL performance of the original luminescence, which is of great significance to improve the sensitivity of the ECL sensor.<sup>21,22</sup> Therefore, improving the synthesis method and optimizing the functional structure to obtain functionalized doped graphene quantum dots with controllable morphology and higher efficiency are an effective means to improve the ECL system. Traditional ECL sensors for Hg<sup>2+</sup> mostly rely on the action of the

Laboratory of Pharmacy and Chemistry, Laboratory of Tissue and Cell Biology, Lab Teaching & Management Centre, Chongqing Medical University, Chongqing 401331, China. E-mail: zhushu@cqmu.edu.cn

<sup>†</sup> Electronic supplementary information (ESI) available. See https://doi.org/10.1039/d2ay00297c

<sup>‡</sup> These authors contributed equally to this work.

luminescence system and DNA. However, their complex preparation process and high cost limit their further application.<sup>23</sup>

Inspired by the above, we proposed to introduce the low toxicity reagent dithiothreitol combined with zinc into graphene quantum dots by a one-step hydrothermal method to improve their performance. By optimizing the doping ratio experiment, the new luminophor doped graphene quantum dots by virtue of the affinity of dithiothreitol with metal mercury ions were applied to construct an efficient ECL sensor with good selectivity and high sensitivity. Moreover, ultraviolet spectrophotometry (UV-vis) detection is extended based on the excellent optical performance of the material and the powerful capturing capacity for mercury ions. Meanwhile, visual detection of mercury ions was also attempted. The proposed sensor shows good performance for mercury ion detection and can also be used for real samples. It provides great potential for the development of fast and simple sensors.

## Experimental section

#### **Reagents and apparatus**

Dithiothreitol (DTT), dicyandiamide and poly(vinylpyrrolidone) (PVP) were obtained from Sigma-Aldrich Trading Co. Ltd (Shanghai, China). Metal salts (NaCl, MgSO<sub>4</sub>, Mn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, NiSO<sub>4</sub>·6H<sub>2</sub>O, ZnSO<sub>4</sub>·7H<sub>2</sub>O, Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O, Pb(NO<sub>3</sub>)<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, FeCl<sub>3</sub>·6H<sub>2</sub>O and HgCl<sub>2</sub>) were purchased from Sino-Pharm Chemical Reagent Co. Ltd (Shanghai, China). Gold chloride tetrahydrate (HAuCl<sub>4</sub>·4H<sub>2</sub>O, 99.99%) was obtained from Aladdin Reagent Co. Ltd. (Shanghai, China). PBS solution (0.1 M, pH 7.4) containing 0.1 M KCl was prepared from the stock solutions of 0.1 M Na<sub>2</sub>HPO<sub>4</sub>, 0.1 M KH<sub>2</sub>PO<sub>4</sub> and KCI. The K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> solution (0.1 M, pH 7.4) was prepared with PBS solution. Ultrapure water was used for all experiments.

#### Apparatus

An MPI electrochemiluminescence analyzer (MPI-A, Xi'an Remax Electronics Co. Ltd., China) was employed to record the ECL signals. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) analyses were performed with a CHI electrochemical analyzer (CHI 660E, Shanghai Chenhua Apparatus Inc., China). Employing a conventional three-electrode system, the working electrode was a glassy carbon electrode (GCE, 4 mm in diameter), the reference electrode was Ag/ AgCl soaked in saturated KCl solution, and the auxiliary electrode was a platinum wire. Transmission electron microscopy (TEM) measurements were performed on a JEOL JEM-2010 (200 kV). Fourier transform infrared (FT-IR) spectroscopy was performed on a Nicolet 5700 (USA) with KBr pellets to study the characteristic functional groups on the surface. Ultravioletvisible (UV-vis) absorption spectra and excitation and emission spectra were recorded on a 2450 UV-vis spectrometer (Shimadzu, Japan) and a fluorescence spectrophotometer (SpectraMax iD3, Molecular Devices), respectively. The zeta potentials were measured by dynamic light scattering (DLS) using a NanoBrook Omni instrument (Brookhaven).

#### Synthesis of ZnNCs-NGQDs

First, 1 mL of PVP solution ( $60 \text{ mg mL}^{-1}$ ) and DTT solution (0.1 M) were mixed with ZnSO<sub>4</sub> (0.5 mL, 0.1 M) under stirring for 10 min, and the pH was adjusted to 5–6 using NaOH (0.1 M). Subsequently, white solid precipitates were obtained, which were purified for 10 minutes with ultrapure water at 8000 rpm, and the obtained DTT-Zn was re-dispersed in 2.5 mL ultrapure water.

0.5200 g trisodium citrate dihydrate and 0.6003 g urea were dissolved in 11.2 mL ultrapure water and stirred to form a clear solution with different amounts of DTT–Zn suspension. The solution was transferred into a 50 mL Teflon lined stainless steel autoclave and heated for 8 h at 160 °C. The final product, ZnNCs–NGQDs, was collected by adding ethanol into the solution and upon washing three times. The solid can be easily redispersed in water, and ZnNCs–NGQD suspension was obtained for use. The volume of the final solution is 6 mL. The NGQDs were obtained without DTT–Zn.

#### Fabrication of the proposed solid state ECL sensor

The glassy carbon electrode (GCE) was polished with 1.0, 0.3, and 0.05  $\mu$ m  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> slurry on chamois leather. After sonicating in nitric acid solution, ethanol and ultrapure water for 1 min, respectively, the electrode was dried in air to obtain a specular surface. Then, the clean surfaces of electrodes were electrodeposited by immersing into 2 mL of the precursor 1% HAuCl<sub>4</sub> solution and applying a constant potential of -0.2 V (AuNPs/GCE). Following this, 10  $\mu$ L of ZnNCs–NGQD suspension was dropped onto the surface of the deposited gold film and dried in air (ZnNCs–NGQDs/AuNPs/GCE). The fabrication of the proposed sensor is shown in Scheme 1A.



Scheme 1 (A) Fabrication process and the determination mechanisms of the electrochemiluminescence sensor. (B) The determination mechanisms of UV-vis.

# **Results and discussion**

#### Characterization of the prepared nanocomposites

In order to prepare ECL nanomaterials with high luminescence efficiency, we investigated the effects of different amounts of DDT-Zn on the properties of ZnNCs-NGQDs (Table 1). The results of the ECL intensity of the modified electrodes (ZnNCs-NGQDs/AuNPs/GCE) showed that the highest ECL intensity was obtained in the presence of 800 µL DDT-Zn. This is because the luminescence of quantum dots mainly comes from vacancy defects. A certain amount of DDT-Zn reduces the vacancy selfhealing ability in its synthesis.24 While excessive DDT-Zn occupies a large number of vacancies, at the same time, it makes the uncoordinated surface atomic defects with the quenching effect dominant, so as to quench its luminescence.25,26 The zeta potentiometric results also show that the doped quantum dots have good stability at 400 µL and 800 µL. Considering the above factors and the yield, ZnNCs-NGQDs synthesized with 800 µL addition were used in subsequent experiments.

The morphology of the NGQDs and ZnNCs–NGQDs was characterized by TEM. As shown in Fig. 1A, NGQDs tend to gather and distribute unevenly with an average particle size of 5 nm. The TEM image of ZnNCs–NGQDs (Fig. 1B) indicates that the addition of DTT–Zn significantly improved the particle size and uniformity. The EDS spectrum of ZnNCs–NGQDs (Fig. 1C) reveals the components of the nanomaterial and indicates that the modification of DTT–Zn was successful.

FT-IR spectra (Fig. 1D) were used to characterize the functional groups of the NGQDs (a), DTT-Zn (b) and ZnNCs-NGQDs (c). A broad peak at 3316 cm<sup>-1</sup> of the above three substances reflected the vibration of -OH.<sup>27</sup> The absorption peaks at 1655

Table 1 The effects of different amounts of DDT–Zn on the properties of ZnNCs–NGQDs

View Article Online

Paper

Sample	Zn–DTT amount (μL)	Zeta potential (mv)	Relative yield	ECL intensity (a.u.)
A	0	-22.47	Standard	4240.9
В	400	-43.96	Low	8327.3
С	800	-31.21	High	12500.2
D	1200	-24.36	High	11004.3
Е	1600	-19.57	High	10840.1
F	2000	-16.73	Low	4643.7

and 1077 cm<sup>-1</sup> could be assigned to the stretching vibration of the -C=O and C–O groups, respectively. The peak at 1384 cm<sup>-1</sup> corresponds to the C–N bond, suggesting the existence of N-related bonds.<sup>28</sup> Weak absorption peaks at 620 cm<sup>-1</sup> belong to the vibrational mode of C–S and were distinguishable in the FT-IR spectra between NGQDs and ZnNCs–NGQDs.<sup>28</sup>

In the UV-vis spectra of the NGQDs (Fig. 1E(a)), one remarkable peak assigned to the  $n \rightarrow \pi^*$  conjugate structure of aromatic C=N domains is observed at 288 nm,<sup>29</sup> while DTT-Zn exhibited an absorption band at 333 nm (b), assigned to the  $n \rightarrow \pi^*$  conjugate structure of aromatic C=S domains, which is consistent with previous reports of DTT metal complexes.<sup>30</sup> ZnNCs-NGQDs showed both absorption bands at 288 nm and 333 nm (c), originating from the constituting components DTT-Zn and NGQDs. In Fig. 1F, the maximum excitation wavelength and maximum emission wavelength of NGQDs were at  $\lambda = 350$  and 461 nm, while the corresponding wavelengths of ZnNCs-NGQDs were at  $\lambda = 412$  and 480 nm, and the fluorescence intensity was significantly red shifted. This is because zinc participates in the coordination of surface functional groups,



Fig. 1 (A) TEM images of NGQDs. (B) TEM images of ZnNCs–NGQDs. (C) EDS mapping of ZnNCs–NGQDs. (D) FTIR spectra of (a) NGQDs, (b) DTT–Zn and (c) ZnNCs–NGQDs. (E) UV-vis absorption spectra of (a) NGQDs, (b) DTT–Zn and (c) ZnNCs–NGQDs. (F) FL spectra of (a) NGQDs and (b) ZnNCs–NGQDs (inset: the corresponding photographs under UV light illumination at 365 nm).

which effectively improve the radiation recombination process of electrons and holes, thus improving the fluorescence intensity and producing a red shift.<sup>31</sup>

#### Optimization of experimental conditions

Owing to the excellent ability of metal nanoparticles in enhancing ECL intensity and easy binding with multi-functional groups, we compared the modified electrodes with AuNPs, PtNPs and Au–PtNPs as the substrate, respectively. As shown in Fig. 2A, the modified electrode based on AuNPs has an obvious advantage due to its stronger bond with the thiol group.<sup>32,33</sup> Therefore, AuNPs are chosen as the base of modified electrodes.

In order to optimize the substrate conducive to improving the sensitivity, the effect of the electrodeposition time of the AuNPs was also investigated in the range 30–90 s (Fig. 2B). An obvious high and stable ECL intensity appeared at 60 s, and similar intensities were observed from 60 s to 90 s. Therefore, 60 s was used as the optimal electrodeposition time in further experiments.

The ECL mechanism with  $K_2S_2O_8$  as co-reactant means that when a negative potential is applied to the electrode, the coexisting substance rapidly decomposes to produce a high-energy free radical intermediate  $SO_4$ <sup>--</sup>, and then the ECL reagent reacts with  $SO_4$ <sup>--</sup> to form the excited state of the luminescent substance and luminesces through relaxation. In Fig. 2C, the ECL response of modified electrodes ZnNCs-NGQDs/AuNPs/ GCE gradually increased with  $K_2S_2O_8$  concentration between 10 and 70 mM, and tended to plateau, because an increasing amount of  $SO_4$ .<sup>-</sup> was generated with an increase in  $K_2S_2O_8$ , and then it reaches equilibrium. Thus, 50 mM  $K_2S_2O_8$  was chosen as the optimal concentration for the ECL system.

In this work, an ECL analyzer was applied to show detailed information on ECL signals of different modified electrodes (Fig. 3C). No ECL signal is obtained on the bare electrode (a). When electrodes were modified with AuNPs, only low signals were obtained (b). The signal of NGQDs/AuNPs/GCE (c) was lower than that of ZnNCs-NGQDs/AuNPs/GCE (d), because of the doping effect of ZnNCs-NGQDs.<sup>20,34</sup>

#### ECL mechanism

The ECL mechanisms of the sensitive quenching effect for  $Hg^{2+}$  can be explained as follows: in the absence of  $Hg^{2+}$ , the ZnNCs-GQD nanocomposite can directly obtain external electrons from the working electrode and generate negatively charged anion-radical ZnNCs-NGQDs<sup>--</sup> (eqn (1)), while  $S_2O_8^{2-}$  was electrolyzed into  $SO_4^{--}$  and  $SO_4^{2-}$  (eqn (2)). The anion-radical  $SO_4^{--}$  has a strong oxidation potential, and by capturing an electron from ZnNCs-NGQDs<sup>--</sup>, it can bring the latter substance into the excited state ZnNCs-NGQDs<sup>\*</sup> (eqn (3)). Upon the transition from the excited state back to the ground state, the ZnNCs-NGQD nanocomposite generates an ECL signal, as shown in eqn (4). Alternatively,  $SO_4^{--}$  can directly oxidize ZnNCs-NGQDs into ZnNCs-NGQDs<sup>+</sup> (eqn (5)), which react with ZnNCs-NGQDs<sup>--</sup> to generate ZnNCs-NGQDs (eqn (5) and (6)), followed by their transition to the ground state and the generation



Fig. 2 Optimization of experimental conditions: (A) comparison of the ECL response with modified electrodes (a) ZnNCs-NGQDs/PtNPs/GCE, (b) ZnNCs-NGQDs/Au-PtNPs/GCE and (c) ZnNCs-NGQDs/AuNPs/GCE. (B) Effects of the electrodeposition time of the AuNPs: (a) 30 s, (b) 45 s, (c) 60 s, (d) 75 s, and (e) 90 s. (C) Effect of the  $K_2S_2O_8$  concentration from 10 to 70 mM.



**Fig. 3** (A) CVs and (B) EIS spectra of the different modified electrodes in 5.0 mM  $[Fe(CN)_6]^{3-/4-}$  (1 : 1) solution: (a) bare GCE, (b) AuNPs/GCE, and (c) ZnNCs–NGQDs/AuNPs/GCE. (C) ECL curves of the different modified electrodes in PBS containing 50 mM S<sub>2</sub>O<sub>8</sub><sup>2-</sup>: (a) bare GCE, (b) AuNPs/GCE, (c) NGQD/AuNPs/GCE and (d) ZnNCs–NGQD/AuNPs/GCE.

of ECL (eqn (4)). As a large amount of  $S_2O_8^{2-}$  is present and the reduction potential of  $S_2O_8^{2-}$  is much more than that of  $Hg^{2+}$ ,  $S_2O_8^{2-}$  is reduced prior to  $Hg^{2+}$  under the set potential. The quenching of the ECL signal was observed owing to the chelation of  $Hg^{2+}$  through the free S–H groups available on the surface of ZnNCs (eqn (7)).<sup>35</sup> The change of FL signal intensity before and after the addition of  $Hg^{2+}$  and subsequent visual attempts for mercury ion detection prove that quenching is due to the complexation of  $Hg^{2+}$  with ZnNCs–NGQDs (Fig. S1† and 5D). This has partially deactivated ZnNCs–NGQDs and suppressed reaction (1), which appeared to be dependent on the  $Hg^{2+}$  concentration over a rather broad range.

$$ZnNCs-NGQDs + e^- \rightarrow ZnNCs-NGQDs^{--}$$
 (1)

$$S_2 O_8^{2-} \to S O_4^{\cdot -} + S O_4^{2-}$$
 (2)

$$ZnNCs-NGQDs^{-} + SO_4^{-} \rightarrow ZnNCs-NGQDs^{*} + SO_4^{2-}$$
 (3)

$$ZnNCs-NGQDs^* \rightarrow ZnNCs-NGQDs + h\nu$$
(4)

$$ZnNCs-NGQDs + SO_4^{-} \rightarrow ZnNCs-NGQDs^+ + SO_4^{2-}$$
 (5)

$$ZnNCs-NGQDs^{+} + ZnNCs-NGQDs^{-} \rightarrow ZnNCs-NGQDs^{*} + ZnNCs-NGQDs$$
 (6)

$$Hg^{2+} + ZnNCs-NGQDs \rightarrow Hg^{2+}-ZnNCs-NGQDs$$
 (7)

#### ECL and UV-vis spectral detection

As shown in Fig. 4A, to estimate the performance of the ECL sensor, different concentrations of Hg<sup>2+</sup> were monitored. The ECL intensity displays a gradual decrease with an elevated concentration of Hg<sup>2+</sup> from 1.0 mM to 10 pM. The linear regression equation is expressed as  $\Delta I = 1149.8 \text{ lg } C_{\text{Hg}^{2+}} + 13 \text{ 644}$  ( $R^2 = 0.9986$ ), where  $\Delta I$  and *C* represent the ECL intensity of difference values ( $\Delta I = I_0 - I$ , where  $I_0$  and *I* represent the ECL intensity in the absence and presence of the quencher Hg<sup>2+</sup>, respectively) and the concentration of Hg<sup>2+</sup>, respectively. The detection limit is 3 pM (S/N = 3). The experimental results showed high sensitivity. Table 2 shows the result of comparison with other methods and ECL techniques for the detection of Hg<sup>2+</sup>. The sensor in this work was superior to others with a wider linear response range and a lower detection limit.

The corresponding UV-vis spectra with different  $Hg^{2+}$  concentrations were recorded (Fig. 4b). As the  $Hg^{2+}$  concentration increased from 0.1 nM to 0.1 mM, the absorbance decreased from 1.197 to 0.766. The linear regression equation is expressed as  $A = 0.5294 - 0.0674 \lg C$  ( $R^2 = 0.9985$ ), where A and C represent the absorbance intensity and the concentration of  $Hg^{2+}$ , respectively. The detection limit is 33 pM (S/N = 3).

#### Stability, reproducibility and selectivity of the sensor

The stability of the ECL sensor for  $Hg^{2+}$  is presented in Fig. 5A(a). The precision of the sensor was evaluated by



**Fig. 4** (A) ECL response for (a) different concentrations of  $Hg^{2+}$  (from (a) to (j) 1.0 mM, 0.1 mM, 10  $\mu$ M, 1.0  $\mu$ M, 0.1  $\mu$ M, 10 nM, 1.0 nM, 0.1 nM, 10 pM, and 0 M), and (b) the calibration curve. (B) UV-vis spectra for (a) different concentrations of  $Hg^{2+}$  (from (a) to (h) 0.1 mM, 10  $\mu$ M, 1.0  $\mu$ M, 0.1  $\mu$ M, 0.1  $\mu$ M, 1.0 nM, 1.0 nM, 0.1  $\mu$ M, 1.0  $\mu$ M, 0.1  $\mu$ M, 0.1

1

Table 2	Comparison of	sensitivities of	this work with	other methods a	and ECL techn	iaues for the o	determination of	of Ha <sup>2+</sup>
								· J

Nanocomposites	Linear range (nM)	$LOD^{a}$ (nM)	Method	Ref.
TMT-AuNPs	5-1000	2.8	ECL	36
DTT/C-AuNCs	50-1000	8.7	ECL	37
TT-CuNCs/CNNSs	0.05-10	0.01	ECL	38
SiNPs/AuNCs	20-24 000	5.6	$\mathbf{FL}$	39
Cu-MOF	0.1-50	0.0633	DPV	40
ZnNCs-NCQDs	$0.01 - 1 \ 000 \ 000$	0.003	ECL	This work
<sup><i>a</i></sup> The calculation method of	LOD is the same as that in this expe	riment.		

calculating the intra- and inter-assay variation coefficients (n =5). The experimental results indicated that the intra-assay variations were less than 5% at different concentrations, while the inter-assay variations using nanoparticles from different batches were also less than 5% at corresponding concentrations (Fig. 5A(b)). The sensor exhibited satisfactory stability and reproducibility. In addition, the long-term storage stability was studied by recording the ECL intensities of the electrodes stored in a refrigerator (4 °C) for 5 weeks. Fig. 5A(c) shows that the ECL intensity retained approximately 96.8% of its initial intensity value after 5 weeks, suggesting that the sensor is extremely stable. The selectivity of the ECL sensor was tested by using metal ions Na<sup>+</sup>, K<sup>+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Hg<sup>2+</sup>, Fe<sup>3+</sup> and  $Cr^{3+}$  with a concentration of 1.0  $\mu$ M. As shown in Fig. 5B, the results exhibited no significant ECL responses compared with that of Hg<sup>2+</sup>, demonstrating a satisfactory selectivity.

#### Visual attempts for mercury ion detection

Considering the strong capture ability of doped quantum dots for mercury ions, we tried to explore a convenient and fast way for visual detection (Fig. 5C): a solution of interfering metal ions with a concentration of 1.0 mM was prepared. And then, 20  $\mu$ L of ZnNCs–NGQD solution were added, respectively. After a while, the solution containing  $Hg^{2+}$  changed from brown to clear colorless and showed obvious precipitation. We also tested the effect of different concentrations of  $Hg^{2+}$  (1.0 mM, 0.1 mM and 0.01 mM) compared with NGQDs (Fig. 5D). The results show that the un-doped quantum dots NGQDs have no adsorption capacity, and the differentiated presentation for different concentrations of  $Hg^{2+}$  provides the possibility for visual detection.

#### Analytical application

For the demonstration of the practical use of the ECL sensor, both lake and tap water samples were tested for their  $Hg^{2+}$ contents. The lake water samples were taken from Zimu lake of Chongqing Medical University (Chongqing, China), and the tap water was collected from our laboratory. Both samples were filtered through a 0.22 µm membrane to remove any suspended impurities and diluted 1 : 1 (by volume) with 0.1 M PBS (pH 7.4) containing 50 mM K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>. Then, the water samples were spiked with 100 nM, 1.0 nM and 0.01 nM Hg<sup>2+</sup> standard solutions, respectively, and analyzed by using the ECL sensor. The obtained results were compared with the data obtained from the DPV method<sup>41</sup> and are summarized in Table 3. The result showed an acceptable agreement with a RSD less than 5%,



**Fig. 5** (A) Stability and reproducibility of the sensor: (a) stability of the proposed ECL sensor without  $Hg^{2+}$  (0 M), and (b) stability of the proposed ECL sensor toward  $Hg^{2+}$  (0.01 nM); (c) the reproducibility tests of five modified electrodes for detection of  $Hg^{2+}$  (0.01 nM), and (d) long-term storage stability of the method upon incubation with 0.01 nM  $Hg^{2+}$ . (B) Selectivity evaluation of the sensor against other metal ions (1.0  $\mu$ M). (C) Visual attempts *via* different metal ions interacting with ZnNCs–NGQD. (D) Visual attempts: (a)  $Hg^{2+}$  interacting with NGQDs, and (b) different concentrations of  $Hg^{2+}$  interacting with ZnNCs–NGQD.

 Table 3 Detection of Hg<sup>2+</sup> in aqueous samples by the proposed method

Sample	Added (nM)	This work (nM)	DPV (nM)	RSD (%)	Recovery <sup>a</sup> (%)
Tap water	100	102	101	0.07	102
	1.0	1.07	1.05	0.26	105
	0.01	0.0096	0.0102	0.73	96
Lake water	100	101	102	0.12	101
	1.0	0.98	1.03	0.34	98
	0.01	0.0110	0.0105	1.12	105
<sup><i>a</i></sup> Average value fro	m three separate measure	ments.			

which indicated that the proposed sensor is available for application for detecting  $Hg^{2+}$  in real water samples.

# Conclusions

In conclusion, a novel analytical platform for the visual, sensitive, and reliable analysis of mercury ions was successfully developed using functionalized doped quantum dots. The newly synthesized nano-material, ZnNCs-NGQDs, by a simple and convenient one-pot method not only is an excellent ECL luminophor, but also a good mercury ion selector. Based on this, two kinds of sensitive ECL and visualization sensors are developed simultaneously. The sensor exhibited a stronger signal for Hg<sup>2+</sup> detection. In addition, the sensor incorporated the advantages of specificity and simplicity, which greatly improved its sensitively and selectivity. Furthermore, the feasibility of this proposed sensor was demonstrated by detecting Hg<sup>2+</sup> in actual water samples with good reproducibility, providing a new avenue in the establishment of sensors for detecting Hg<sup>2+</sup> and other small molecules. This work strongly shows novel material design ideas and application exploration for rapid, simple and sensitive sensors.

### Author contributions

Zhipeng Wu: data curation, conceptualization, formal analysis, writing – original draft and visualization. Chenglin Dai: methodology, formal analysis, software and visualization. Yiwu Wang: conceptualization, methodology and resources. Lianju Ma: conceptualization, resources and supervision. Guangchao Zang: resources and supervision. Qian Liu; methodology and supervision. Shu Zhu: methodology, supervision, resources, and writing – review & editing.

# Conflicts of interest

There are no conflicts to declare.

# Acknowledgements

The authors gratefully acknowledge financial support for this study by the Innovative Talent Promotion Program in Lab Teaching & Management Centre of Chongqing Medical University (LTMC201903 and LTMC202104), the Project of Tutorial System of Medical Undergraduate in Lab Teaching & Management Centre of Chongqing Medical University (LTMCMTS201903 and LTMCMTS202121), the Project of Scientific Research and Innovative Experiment for College Student of Chongqing Medical University (SRIEP201966), and CQMU Program for Youth Innovation in Future Medicine (W0015).

## Notes and references

- 1 M. M. Correia, M. C. Chammas, J. D. Zavariz, A. Arata, L. C. Martins, S. Marui and L. A. Pereira, *Int. Arch. Occup. Environ. Health*, 2020, **93**, 491–502.
- 2 M. Zeng, M. Chen, D. Huang, S. Lei, X. Zhang, L. Wang and Z. Cheng, *Mater. Horiz.*, 2021, **8**, 758–802.
- 3 Y. Li, Q. Lin, Z. Zhang, T. Wei, B. Shi, H. Yao and Y. M. Zhang, *Nanoscale*, 2021, **13**, 9172–9176.
- 4 Z. He, T. Kang, L. Lu and S. Cheng, *Anal. Methods*, 2020, **12**, 491–498.
- 5 Y. Ma, Y. J. Yu, X. Y. Mu, C. Yu, Y. Zhou, J. Chen, S. T. Zheng and J. L. He, *J. Hazard. Mater.*, 2021, **415**, 125538–125545.
- 6 F. Yu, P. Luo, Y. Chen, H. Jiang and X. Wang, *Anal. Methods*, 2021, **13**, 2575–2585.
- 7 U. Ghorui, J. Satra, P. Mondal, S. Mardanya, A. Sarkar, D. N. Srivastava, B. Adhikary and A. Mondal, *Mater. Adv.*, 2021, 2, 4041–4057.
- 8 W. Li, B. Ju and S. Zhang, Cellulose, 2019, 26, 4971-4985.
- 9 J. Li, Y. Liu, Y. J. Ai, A. Alsaedi, T. Hayat and X. K. Wang, *Chem. Eng. J.*, 2020, **388**, 790–802.
- 10 H. Lu, J. J. Xu, H. Zhou and H. Y. Chen, *TrAC, Trends Anal. Chem.*, 2020, **122**, 115746–115757.
- 11 C. Ma, Y. Cao, X. D. Gou and J. J. Zhu, *Anal. Chem.*, 2020, **92**, 431–454.
- 12 L. Q. Yang, C. R. De-Jager, J. R. Adsetts, K. Chu, K. H. Liu, C. Y. Zhang and Z. F. Ding, *Anal. Chem.*, 2021, 93, 12409– 12416.
- 13 B. G. Zhang, J. L. Wang, L. Ping, Y. F. Zhong and F. Z. Li, *Sci. Adv. Mater.*, 2020, **12**, 1312–1322.
- 14 H. J. Chen, X. Liu, C. Yin, W. Li, X. D. Qin and C. Y. Chen, *Analyst*, 2019, **144**, 5215–5222.
- 15 J. Wang, C. Lu, T. T. Chen, L. P. Hu, Y. K. Du, Y. Yao and M. C. Goh, *Nanophotonics*, 2020, **9**, 3831–3839.
- 16 S. Tajik, Z. Dourandish, K. Zhang, H. Beitollahi, Q. V. Le and H. W. Jang, *RSC Adv.*, 2020, **10**, 15406–15429.

- 17 R. Z. Zhang, J. R. Adsetts, Y. T. Nie, X. H. Sun and Z. F. Ding, *Carbon*, 2018, **129**, 45–53.
- 18 B. Babarniri, D. Bahari and A. Salimi, *Biosens. Bioelectron.*, 2019, **142**, 111530–111542.
- 19 C. I. Chukwuma, S. S. Mashele, K. C. Eze, G. R. Matowane, S. M. Islam, S. L. Bonnet, A. E. M. Noreljaleel and L. M. Ramorobi, *Pharmacol. Res.*, 2020, **155**, 104744–104752.
- 20 B. Zhao, X. Y. Chen, P. Cheng, D. Z. Liao, S. P. Yan and Z. H. Jiang, *J. Am. Chem. Soc.*, 2004, **126**, 15394–15395.
- 21 Z. F. Yang, G. Q. Pu, X. M. Ning, Y. L. Wu, Z. Zhang, D. L. Shan and X. Q. Lu, *Chem. Phys.*, 2019, **21**, 10614–10620.
- 22 G. Q. Pu, Z. F. Yang, Y. L. Wu, Z. Wang, Y. Deng, Y. J. Gao, Z. Zhang and X. Q. Lu, *Anal. Chem.*, 2019, **91**, 2319–2328.
- 23 Z. Zhao and X. Zhou, Sens. Actuators, B, 2012, 171, 860-865.
- 24 C. Meyer, C. Kisielowski, R. Erni, M. D. Rossell, M. F. Crommie and A. Zettl, *Nano Lett.*, 2008, 8, 3582–3586.
- 25 Z. B. Zheng, J. T. Li, T. Ma, H. L. Fang, W. C. Ren, J. Chen, J. She, Y. Zhang, F. Liu, H. Chen, S. Deng and N. S. Xu, *Light: Sci. Appl.*, 2017, 6, e17057.
- 26 L. Zhang, C. Kang, G. Zhang, Z. Pan, Z. Huang, S. Xu, H. Rao, H. Liu, S. Wu, X. Wu, X. Li, A. Zhu, X. Zhong and A. K. Y. Jen, *Adv. Funct. Mater.*, 2021, **31**, 2005930.
- 27 X. Wang, R. H. Song, S. X. Teng, M. M. Gao, J. Y. Ni, F. Liu, S. G. Wang and B. Y. Gao, *J. Hazard. Mater.*, 2010, **170**, 431– 437.
- 28 F. Y. Du, L. S. Sun, Q. L. Zen, W. Tan, Z. F. Cheng, G. H. Ruan and J. P. Li, *Sens. Actuators, B*, 2019, **288**, 96–103.

- 29 L. P. Lin, M. C. Rong, S. S. Lu, X. H. Song, Y. X. Zhong, J. W. Yan, Y. R. Wang and X. Chen, *Nanoscale*, 2015, 7, 1872–1878.
- 30 C. Y. Shao, S. X. Xiong, X. Cao, C. Zhang, T. T. Luo and G. Liu, *Microchem. J.*, 2021, 163, 105922–105936.
- 31 Z. Liu, Y. Gong and Z. Fan, J. Lumin., 2016, 175, 129-134.
- 32 Y. R. Li, Y. Guo, R. Long, D. Liu, D. M. Zhao, Y. B. Tan, C. Gao, S. H. Shen and Y. J. Xiong, *Chin. J. Catal.*, 2018, 39, 453-462.
- 33 N. Gan, L. Y. Wang, T. H. Li, F. Wang and Q. L. Jiang, Acta Phys.-Chim. Sin., 2008, 24, 915–920.
- 34 G. Pu, Z. Yang, Y. Wu, Z. Wang, Y. Deng, Y. Gao, Z. Zhang and X. Lu, *Anal. Chem.*, 2019, **91**(3), 2319–2328.
- 35 J. Li, Y. Liu, Y. J. Ai, A. Alsaedi, T. Hayat and X. K. Wang, *Chem. Eng. J.*, 2020, **388**, 124203–124215.
- 36 J. Wang, X. Fang, X. Q. Cui, Y. H. Zhang, H. Zhao, X. J. Li and Y. J. He, *Talanta*, 2018, **188**, 266–272.
- 37 W. Liu, X. Y. Wang, Y. Q. Wang, J. H. Li, D. Z. Shen, Q. Kang and L. X. Chen, *Sens. Actuators, B*, 2018, 262, 810–817.
- 38 H. T. Liu, X. Q. Gao, X. M. Zhuang, C. Y. Tian, Z. G. Wang,
   Y. X. Li and A. L. Rogach, *Analyst*, 2019, 144, 4425–4431.
- 39 F. Ru, P. Du and X. Lu, Anal. Chim. Acta, 2020, 1105, 139-146.
- 40 S. Singh, A. Numan, Y. Q. Zhan, V. Singh, T. V. Hung and N. D. Nam, *J. Hazard. Mater.*, 2020, **399**, 123042–123051.
- 41 Y. S. Zou, Y. L. Zhang, Z. Z. Xie, S. Y. Luo, Y. M. Zeng, Q. Z. Chen, G. K. Liu and Z. Q. Tian, *Talanta*, 2019, 203, 186–193.