

1 Array electrochemiluminescence device for sensitive and
2 selective visualization of Lead in practical food samples

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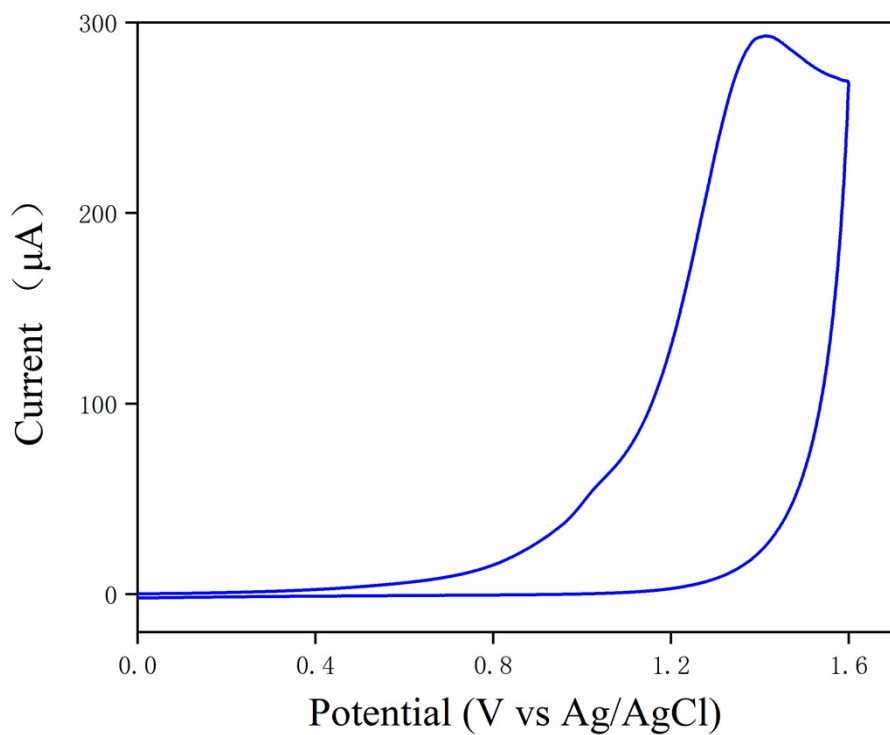
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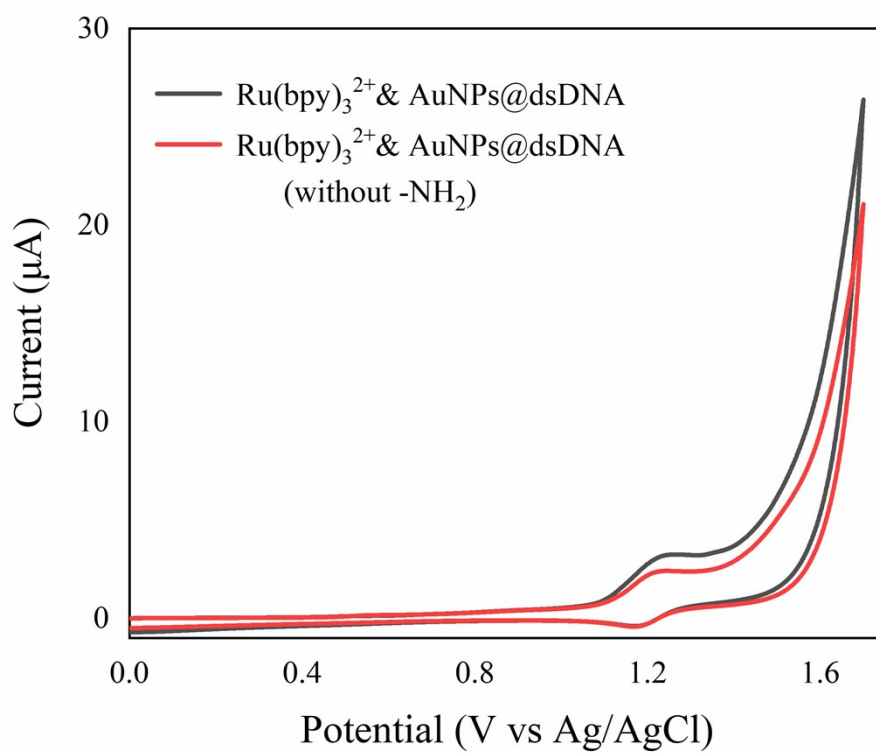
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32 **Figure S1.** The CV data of ethylenediamine in 0.1 M PBS solution, pH = 7.4; scan rate = 100 mV
 33 s⁻¹.

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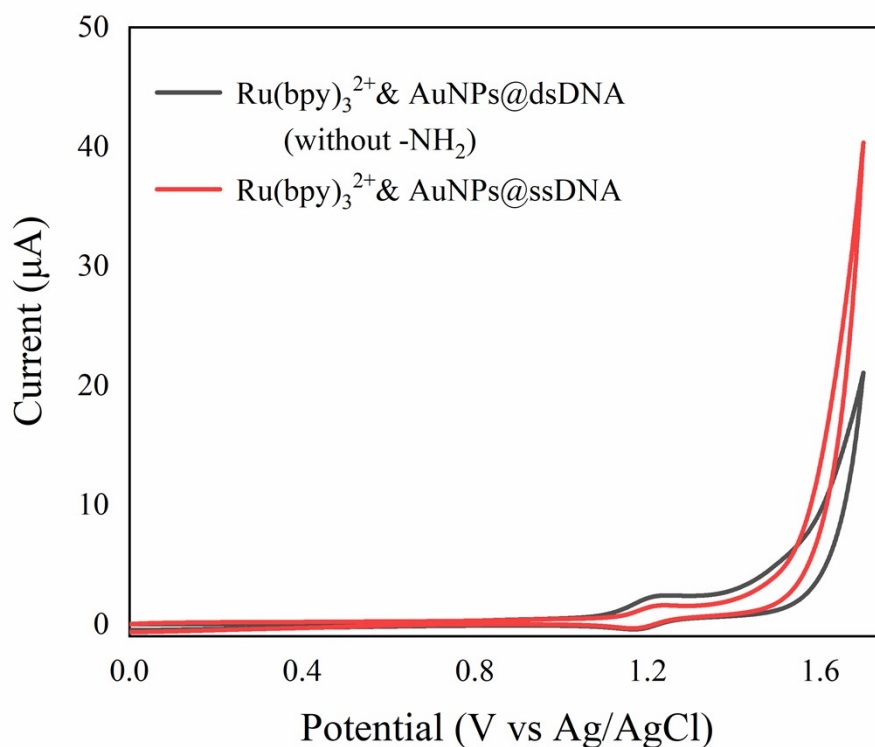
36 **Figure S2.** CV of AuNPs@dsDNA (AuNPs@ssDNA combined with NH₂-ssDNA) and
37 AuNPs@dsDNA without -NH₂ modified GCEs in 0.1 M PBS solution with 1 mM Ru(bpy)₃Cl₂, pH
38 = 7.4. Scan rate = 100 mV s⁻¹.

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44 **Figure S3.** CV of AuNPs@ssDNA and AuNPs@dsDNA without -NH₂ modified GCEs in 0.1 M
45 PBS solution with 1 mM Ru(bpy)₃Cl₂, pH = 7.4. Scan rate = 100 mV s⁻¹.

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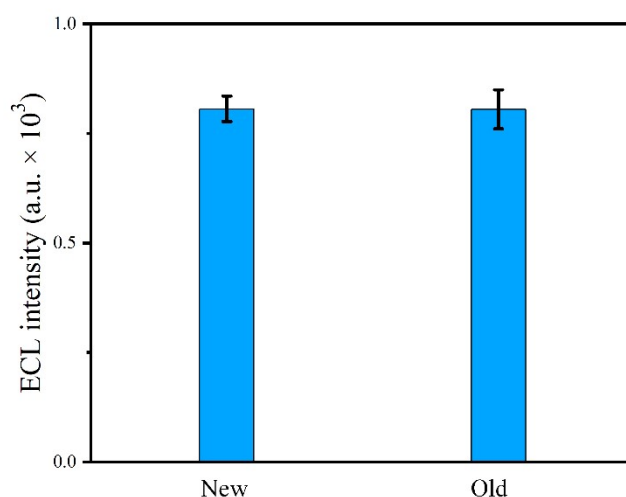
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 61 **Figure S4.** The ECL response of freshly prepared (New) or stored (Old, one month under
 62 room temperature) to the same Pb²⁺ sample (100 ng/L).
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	ECL	ICP-MS
<i>Glycyrrhiza uralensis</i> from Inner Mongolia	22.6 ng/g (R.S.D.:0.6%)	23.8 ng/g (R.S.D.:2.5%)
Lake Water from Dushu Lake	0.279 ng/g (R.S.D.:2.4%)	Out of LOD

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 66 **Figure S5.** The summary of Pb²⁺ concentration in other practical samples determined by
 67 our device and ICP-MS.
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72 **Table S1 The current detection methods for Pb²⁺ and their LODs**

Pb Probes	LODs (µg/L)
C-PFBT Pdots/Fc-DNA/DNA enzyme/GCE ¹	3.522×10 ⁻⁵ (1)
Ru1-17E' 17DS/4-ABA/GE ²	2.900×10 ⁻⁴ (2)
pDNA/MPNs/AuNPs/K ₂ S ₂ O ₈ /GPWE ³	8.288×10 ⁻⁴ (3)
Fe ₃ O ₄ @Au-ssDNA&Ru-NH ₂ /MGCE ⁴	2.072×10 ⁻² (4)
Au NPs electrode/CdS QDs/(Ag/ZnO) ⁵	1.989×10 ⁻⁴ (5)

Pb ²⁺ /S2/S1/SLAg NP-PWE ⁶	414.4	(6)
GQD/L-Cys ⁷	14.5	(7)
P2-rGO-PdAu-GOx ⁸	2.901×10 ⁻²	(8)
AuNPs@nano-C60/GCE ⁹	1.056×10 ⁻⁴	(9)
DPS/Ru-PAMAM-HIFAuNPs /GCE ¹⁰	8.288×10 ⁻⁶	(10)
NH ₂ -SiO ₂ /Ru(bpy) ₃ ²⁺ -UiO66/GCE ¹¹	2.072×10 ⁻⁵	(11)
GR-5 DNAzyme/Ru(phen) ₃ ²⁺ /Au ¹²	1.865×10 ⁻⁴	(12)
TCPP/MCH/DNAzyme/ZnO-Au NPs/GCE ¹³	2.486×10 ⁻⁴	(13)
PTC-NH ₂ /cDNA/MCH/Apt/AuNCs/GCE ¹⁴	1.036×10 ⁻⁵	(14)
CdTe/GO, graphene/AuNPs/ITO ¹⁵	7.874×10 ⁻⁴	(15)
G-quadruplex/P-GO@QDs/GCE ¹⁶	1.865×10 ⁻⁶	(16)
MXene@Au/Ru(bpy) ₃ ²⁺ /GCE ¹⁷	2.590×10 ⁻⁵	(17)
g-C ₃ N ₄ QDs@NPG-S3/ITO ¹⁸	4.144×10 ⁻³	(18)
Ru@AuNPs/Si@CNCs-DNA /NaIO ₄ ¹⁹	2.072×10 ⁻³	(19)
RhB/dsDNA/Pdots/GCE ²⁰	7.873×10 ⁻³	(20)
DNAapt/MCH/cDNA/CNNFs/PCNTs-AuNPs/GCE ²¹	8.288×10 ⁻⁶	(21)
DNAzyme/TBR-NHS/Au ²²	2.279×10 ⁻³	(22)
DNA/2D BP/Ag/AgCl/GCE ²³	5.657×10 ⁻³	(23)
4-CNox/DNAzyme/T30695/MoS ₂ -CdSe@CdS/GCE ²⁴	2.031×10 ⁻⁷	(24)
AgNWs/ S1 and S2-Fc/RuNDs/GCE ²⁵	6.838×10 ⁻⁴	(25)
HKUST-1@rGO@Au/DNAzyme (S1)/CdS QDs/HRP ²⁶	2.072×10 ⁻²	(26)
Fe ₃ O ₄ -Au-G4-QDs ²⁷	2.238×10 ⁻³	(27)

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74 References

- 75 (1) Y. He; X. X. Hu; Z. J. Gong; S. H. Chen; R. Yuan, A novel electrochemiluminescence biosensor
76 based on the self-ECL emission of conjugated polymer dots for lead ion detection. *Microchim. Acta*
77 **2020**, *187* (4), 8.
- 78 (2) F. Ma; B. Sun; H. L. Qi; H. G. Zhang; Q. A. Gao; C. X. Zhang, A signal-on electrogenerated
79 chemiluminescent biosensor for lead ion based on DNAzyme. *Anal. Chim. Acta* **2011**, *683* (2), 234-241.
- 80 (3) L. Zhu; X. Lv; Z. L. Li; H. H. Shi; Y. Zhang; L. N. Zhang; J. H. Yu, All-sealed paper-based

81 electrochemiluminescence platform for on-site determination of lead ions. *Biosens. Bioelectron.* **2021**,
82 *192*, 7.

83 (4) T. T. Hao; C. F. Zhang; H. Lin; W. T. Wei; F. Yang; Y. B. Wu; L. M. Niu; W. J. Kang; Z. Y. Guo,
84 A One-Step Dual-Mode Aptasensor for Subnanomolar Detection of Lead Ions Based on
85 Electrochemiluminescence and Fast Scan Voltammetry. *J. Electrochem. Soc.* **2020**, *167* (12), 8.

86 (5) M. Li; Q. K. Kong; Z. Q. Bian; C. Ma; S. G. Ge; Y. Zhang; J. H. Yu; M. Yan, Ultrasensitive detection
87 of lead ion sensor based on gold nanodendrites modified electrode and electrochemiluminescent
88 quenching of quantum dots by electrocatalytic silver/zinc oxide coupled structures. *Biosens. Bioelectron.*
89 **2015**, *65*, 176-182.

90 (6) Y. Z. Huang; L. Li; Y. Zhang; L. Zhang; S. G. Ge; H. Li; J. Yu, Cerium Dioxide-Mediated Signal
91 "On-Off" by Resonance Energy Transfer on a Lab-On-Paper Device for Ultrasensitive Detection of Lead
92 Ions. *ACS Appl. Mater. Interfaces* **2017**, *9* (38), 32591-32598.

93 (7) Y. Q. Dong; W. R. Tian; S. Y. Ren; R. P. Dai; Y. W. Chi; G. N. Chen, Graphene Quantum Dots/L-
94 Cysteine Coreactant Electrochemiluminescence System and Its Application in Sensing Lead(II) Ions.
95 *ACS Appl. Mater. Interfaces* **2014**, *6* (3), 1646-1651.

96 (8) J. M. Xu; Y. Zhang; L. Li; Q. K. Kong; L. Zhang; S. G. Ge; J. H. Yu, Colorimetric and
97 Electrochemiluminescence Dual-Mode Sensing of Lead Ion Based on Integrated Lab-on-Paper Device.
98 *ACS Appl. Mater. Interfaces* **2018**, *10* (4), 3431-3440.

99 (9) Y. M. Lei; W. X. Huang; M. Zhao; Y. Q. Chai; R. Yuan; Y. Zhuo, Electrochemiluminescence
100 Resonance Energy Transfer System: Mechanism and Application in Ratiometric Aptasensor for Lead
101 Ion. *Anal. Chem.* **2015**, *87* (15), 7787-7794.

102 (10) W. Deng; L. R. Hong; M. Zhao; Y. Zhuo; M. Gao, Electrochemiluminescence-based detection
103 method of lead(II) ion dual enhancement of intermolecular and intramolecular co-reaction. *Analyst* **2015**,
104 *140* (12), 4206-4211.

105 (11) X. M. Shan; T. Pan; Y. T. Pan; W. C. Wang; X. H. Chen; X. L. Shan; Z. D. Chen, Highly Sensitive
106 and Selective Detection of Pb(II) by $\text{NH}_2\text{-SiO}_2/\text{Ru}(\text{bpy})_3^{2+}\text{-UiO66}$ based Solid-state ECL Sensor.
107 *Electroanalysis* **2020**, *32* (3), 462-469.

108 (12) A. Gao; C. X. Tang; X. W. He; X. B. Yin, Electrochemiluminescent lead biosensor based on GR-5
109 lead-dependent DNazyme for $\text{Ru}(\text{phen})_3^{2+}$ intercalation and lead recognition. *Analyst* **2013**, *138* (1),
110 263-268.

111 (13) Q. A. Han; C. Wang; P. K. Liu; G. Zhang; L. Song; Y. Z. Fu, Three kinds of porphyrin dots as near-
112 infrared electrochemiluminescence luminophores: Facile synthesis and biosensing. *Chem. Eng. J.* **2021**,
113 *421*, 9.

114 (14) P. A. Jiang; L. J. Luo; X. H. Liu; W. L. Zhao; X. Y. Bi; L. Luo; L. B. Li; T. Y. You, A potential-
115 resolved ratiometric electrochemiluminescence aptasensor for Pb²⁺: Gold nanoclusters and amino-
116 terminated perylene derivative as both emitters and resonance energy transfer donor-acceptor pair. *Sens.*
117 *Actuator B-Chem.* **2023**, *386*, 8.

118 (15) H. Hai; F. Yang; J. P. Li, Highly sensitive electrochemiluminescence "turn-on" aptamer sensor for
119 lead(II) ion based on the formation of a G-quadruplex on a graphene and gold nanoparticles modified
120 electrode. *Microchim. Acta* **2014**, *181* (9-10), 893-901.

121 (16) H. Y. Song; T. F. Kang; M. F. Jiang; J. J. Zhang; S. Y. Cheng, A novel strategy based on DNAzyme
122 for electrochemiluminescence detection of Pb(II) with P-GO@QDs for signal amplification. *J.*
123 *Electroanal. Chem.* **2017**, *801*, 244-250.

124 (17) H. G. Zhai; Y. Wang; J. Q. Yin; Y. H. Zhang; Q. Guo; X. Sun; Y. M. Guo; Q. Q. Yang; F. L. Li; Y.
125 Y. Zhang, Electrochemiluminescence biosensor for determination of lead(II) ions using signal
126 amplification by Au@SiO₂ and tripropylamine-endonuclease assisted cycling process. *Microchim. Acta*
127 **2022**, *189* (9), 11.

128 (18) Y. Zhang; L. N. Zhang; Q. K. Kong; S. G. Ge; M. Yan; J. H. Yu, Electrochemiluminescence of
129 graphitic carbon nitride and its application in ultrasensitive detection of lead(II) ions. *Anal. Bioanal.*
130 *Chem.* **2016**, *408* (25), 7181-7191.

131 (19) M. Zhang; L. Ge; S. G. Ge; M. Yan; J. H. Yu; J. D. Huang; S. Liu, Three-dimensional paper-based
132 electrochemiluminescence device for simultaneous detection of Pb²⁺ and Hg²⁺ based on potential-control
133 technique. *Biosens. Bioelectron.* **2013**, *41*, 544-550.

134 (20) F. Sun; Z. Y. Wang; Y. Q. Feng; Y. X. Cheng; H. X. Ju; Y. W. Quan, Electrochemiluminescent
135 resonance energy transfer of polymer dots for aptasensing. *Biosens. Bioelectron.* **2018**, *100*, 28-34.

136 (21) Y. J. Peng; Y. Li; L. L. Li; J. J. Zhu, A label-free aptasensor for ultrasensitive Pb²⁺ detection based
137 on electrochemiluminescence resonance energy transfer between carbon nitride nanofibers and
138 Ru(phen)₃²⁺. *J. Hazard. Mater.* **2018**, *359*, 121-128.

139 (22) X. Zhu; Z. Y. Lin; L. F. Chen; B. Qiu; G. A. Chen, A sensitive and specific electrochemiluminescent
140 sensor for lead based on DNAzyme. *Chem. Commun.* **2009**, (40), 6050-6052.

141 (23) Y. H. Wang; H. H. Shi; L. N. Zhang; S. G. Ge; M. L. Xu; X. Wang; J. H. Yu, Two-dimensional
142 black phosphorus nanoflakes: A coreactant-free electrochemiluminescence luminophors for selective
143 Pb^{2+} detection based on resonance energy transfer. *J. Hazard. Mater.* **2021**, *403*, 9.

144 (24) X. L. Du; T. F. Kang; L. P. Lu; S. Y. Cheng, An electrochemiluminescence sensor based on
145 CdSe@CdS functionalized MoS_2 and hemin/G-quadruplex-based DNAzyme biocatalytic precipitation
146 for sensitive detection of Pb(II). *Anal. Methods* **2018**, *10* (1), 51-58.

147 (25) H. J. Wang; Y. H. Song; Y. Q. Chai; R. Yuan, Highly sensitive biosensor based on target induced
148 dual signal amplification to electrochemiluminescent nanoneedles of Ru(II) complex. *Biosens.*
149 *Bioelectron.* **2019**, *140*, 64-68.

150 (26) Y. Zhang; J. M. Xu; S. Zhou; L. Zhu; X. Lv; J. Zhang; L. N. Zhang; P. H. Zhu; J. H. Yu, DNAzyme-
151 Triggered Visual and Ratiometric Electrochemiluminescence Dual-Readout Assay for Pb(II) Based on
152 an Assembled Paper Device. *Anal. Chem.* **2020**, *92* (5), 3874-3881.

153 (27) H. Hai; F. Yang; J. P. Li, Electrochemiluminescence sensor using quantum dots based on a G-
154 quadruplex aptamer for the detection of Pb^{2+} . *RSC Adv.* **2013**, *3* (32), 13144-13148.

155