# Two Novel Manganese–based Phosphomolybdate Compounds as Electrochemical Sensors for the Highly Sensitive Trace Determination of Heavy Metal Cr(VI) Ions

Jinling Wang,‡[a] Xiaohui Liu,‡[a] Zhihan Chang,*[a] Na Xu,*[a] and Xiuli Wang[a]

[a]*College of Chemistry and Materials Engineering, Bohai University, Liaoning Professional Technology Innovation Center of Liaoning Province for Conversion Materials of Solar Cell, Jinzhou 121013, P. R. China.*

## Materials and methods

Chemical medicines were purchased commercially from suppliers. All chemical reactants were used directly. The $H_2SO_4$–$Na_2SO_4$ buffer solutions were prepared by the sulfuric acid and sodium sulfate. The single–crystal diffraction data for compounds **1**–**2** were collected by using a Bruker SMART APEX II CCD diffractometer at 293 K with Mo Kα radiation ($\lambda$ = 0.71073 Å). The Varian 640 FT–IR spectrometer was used for FT–IR spectra (KBr pellets). Powder X–ray diffraction (PXRD) patterns of the samples were measured by a D/teX Ultra diffractometer. Thermogravimetric analyses (TGA) were performed on a Pyris Diamond TGA instrument under a flowing $N_2$ atmosphere with a heating rate of 10 °C/min. Electrochemical experiments and electrochemical impedance spectroscopy (EIS) were received from CHI 760 Instruments. And the electrochemical test used a conventional three–electrode system: the titled compound modified carbon paste electrode as a working electrode, the platinum wire electrode as a counter electrode, and the Ag/AgCl electrode as a reference electrode. UV–vis absorption spectra were collected on an SP 1901 UV–vis spectrophotometer. CCDC: 2216720 and 2216721.

## X–ray crystallography

The structure of compounds **1**−**2** were solved by direct methods and refined finally by full–matrix least–squares on $F^2$ using the SHELX–XL program of the SHELX–XT package.[1–3] The crystal and structure refinement data of compounds **1**−**2** are listed in Table S1. The selected bond lengths and bond angles are shown in Tables S2−S5.

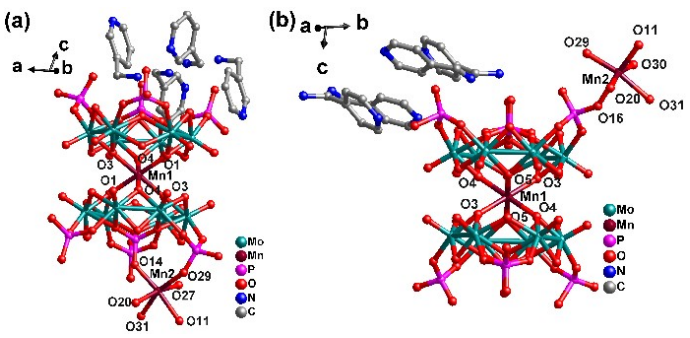


**Fig. S1** Coordination environment diagram of (a) compound **1** and (b) compound **2**. All hydrogen atoms have been omitted for clarity.

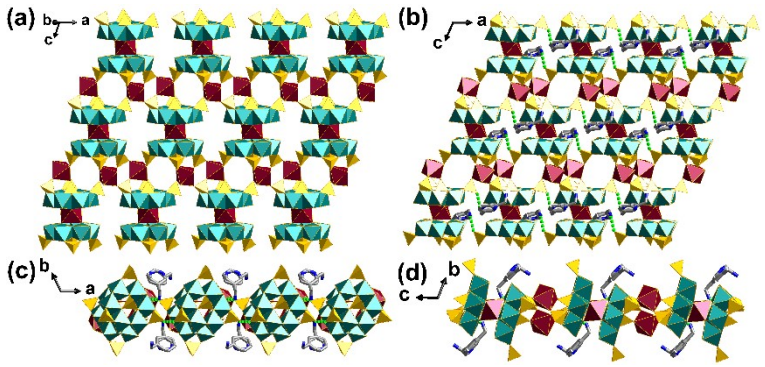


**Fig. S2** (a) The 2D structure diagram of compound **1**. The two hydrogen bonds between compound **1** and the organic ligand form a 3D structure along *b* (b), *c* (c), *a* (d) axis, respectively.

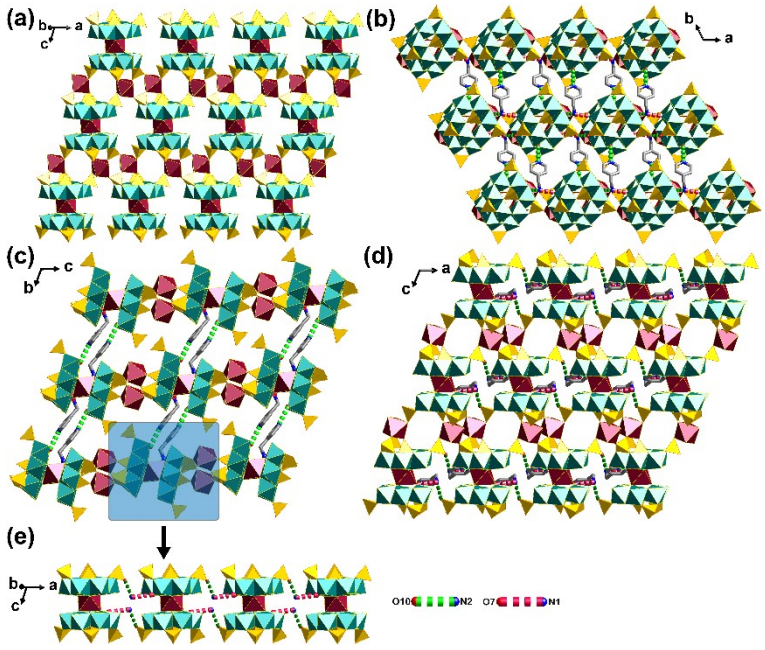


**Fig. S3** (a) The 2D structure diagram of compound **2**. The two hydrogen bonds between compound **2** and the organic ligand form a 3D structure along *c* (b), *a* (c), *b* (d) axis, respectively. (e) Hourglass polyoxoanions interact with organic ligands through two types of hydrogen bonds to form 1D chain along *a* axis.

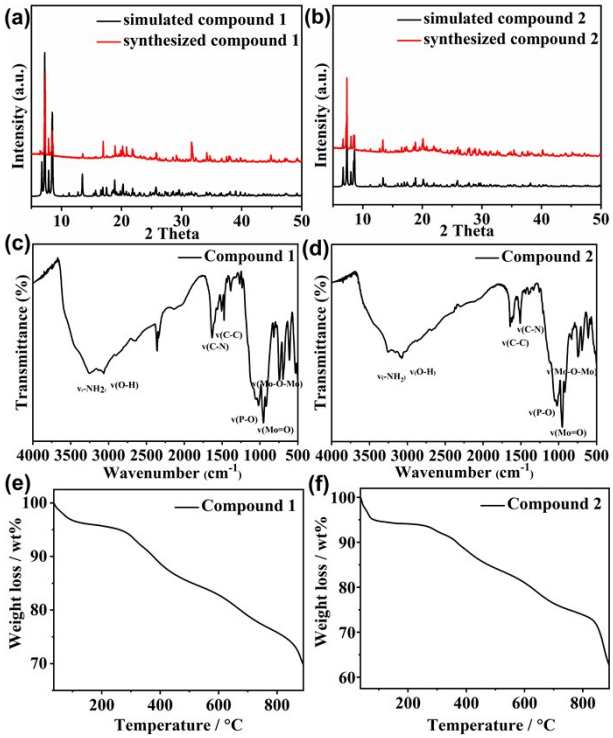


**Fig. S4** (a) The PXRD of compound **1** (b) The PXRD of compound **2** (c) The IR of compound **1** (d) The IR of compound **2** (e) The TGA of compound **1** (f) The TGA of compound **2**.

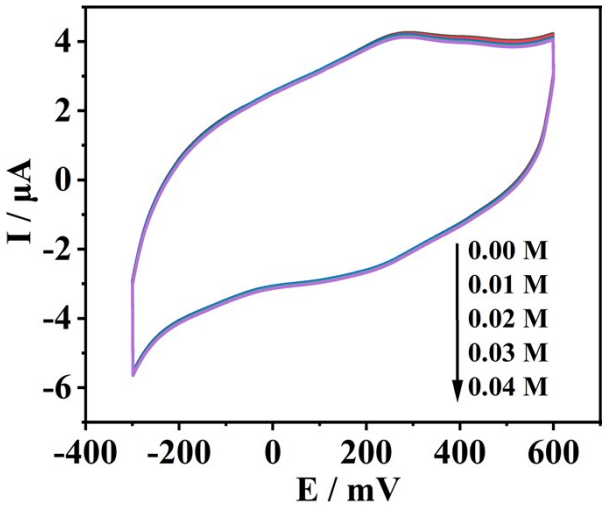


**Fig. S5** The CV curve of bare GP–CPE in a buffer solution containing different concentrations of Cr(VI).

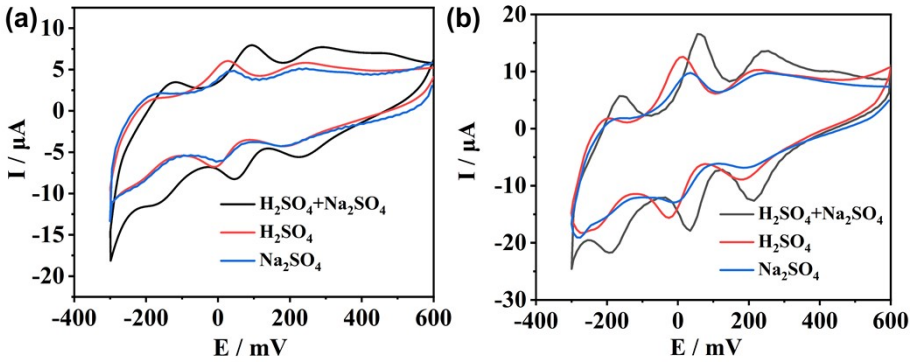


**Fig. S6** CV curves of (a) **1**–CPE, (b) **2**–CPE in different detection solutions.

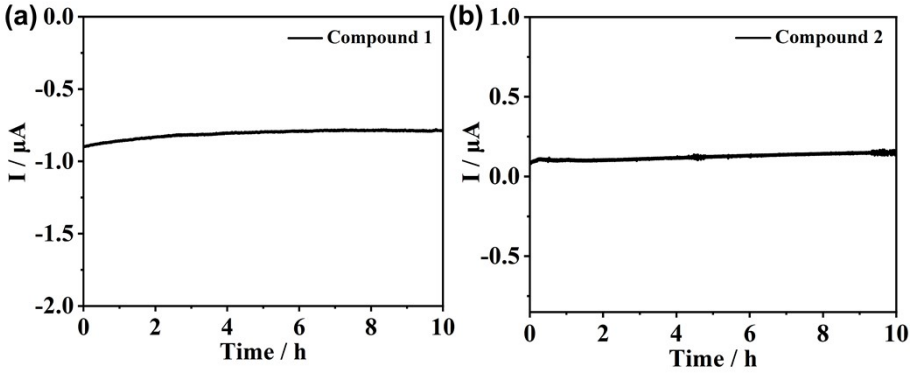


**Fig. S7** The stability of (a) **1**–CPE, (b) **2**–CPE in 500μM Cr(VI) ion was tested in $H_2SO_4$–$Na_2SO_4$ buffer solution.

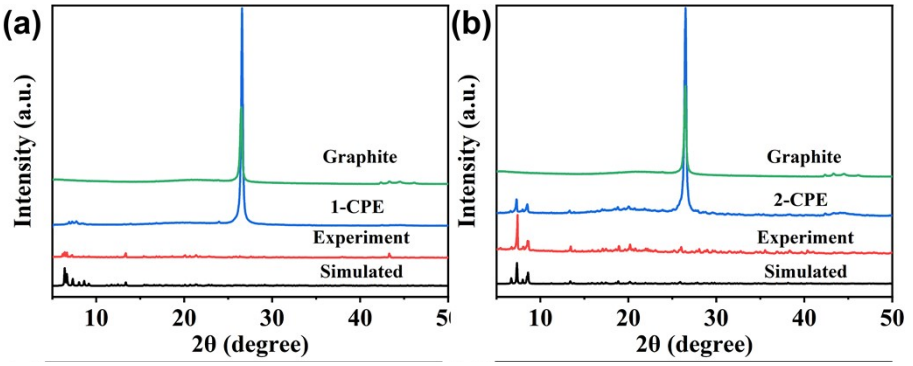


**Fig. S8** The PXRD of (a) **1**–CPE, (b) **2**–CPE and graphite after amperometric detection of Cr(VI) ions over 10 h.

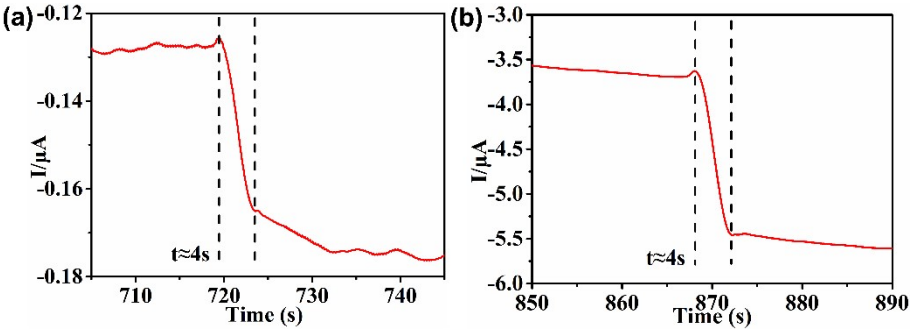


**Fig. S9** Response time diagram of compound **1** (a), **2** (b) for the detection of Cr(VI) in the 0.1 M $H_2SO_4$–0.5 M $Na_2SO_4$ solution.

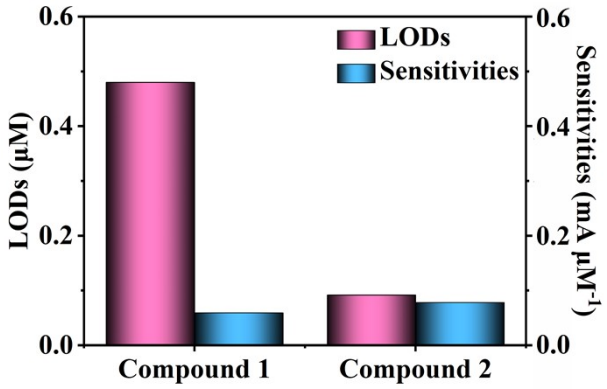


**Fig. S10** The comparison of LOD and sensitivities of compounds **1**–**2** to Cr(VI) ions. (The red part is the detection limit, and the blue part is the sensitivity).

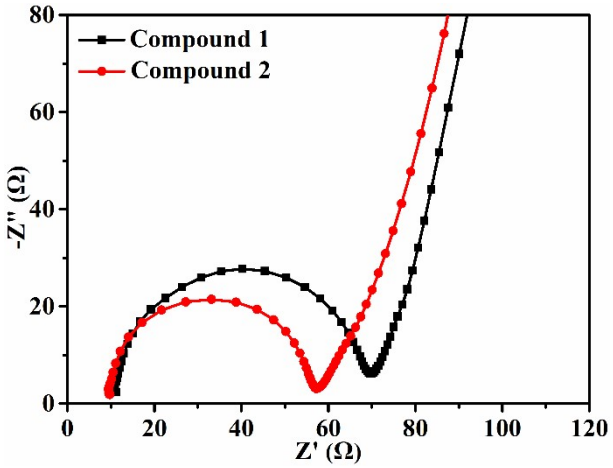


**Fig. S11** Electrochemical impedance spectra (EIS) of the **1**–CPE and **2**–CPE.

**Table S1** Crystal data of compounds **1**–**2**.

| **Compound** | **1** | **2** |
|---|---|---|
| Empirical formula | $C_{24}H_{40}Mn_3Mo_{12}N_8O_{66}P_8$ | $C_{24}H_{34}Mn_3Mo_{12}N_8O_{66}P_8$ |
| Formula weight | 3060.50 | 3054.45 |
| Wavelength | 0.71073 Å | 0.71073 Å |
| Crystal system | Triclinic | Triclinic |
| Space group | $P\bar{1}$ | $P\bar{1}$ |
| *a (Å)* | 12.0309 (8) | 11.9440 (3) |
| *b (Å)* | 14.7291 (9) | 13.7940 (4) |
| *c (Å)* | 13.9974(9) | 14.6825 (4) |
| *α (°)* | 103.2760 (10) | 102.6370 (10) |
| *β (°)* | 106.7290 (10) | 106.00 |
| *γ (°)* | 110.0090 (10) | 110.82 |
| Volume ($Å^3$), Z | 2078.4 (2), 1 | 2033.94 (10), 1 |
| Density (calculated) | 2.445 $Mg/m^3$ | 2.494 $Mg/m^3$ |
| Absorption coefficient | 2.451 $mm^{-1}$ | 2.504 $mm^{-1}$ |
| F(000) | 1467 | 1461 |
| Crystal size ($mm^3$) | 0.24 × 0.22 × 0.2 | 0.24 × 0.22 × 0.2 |
| Goodness–of–fit on $F^2$ | 1.074 | 1.033 |
| Final R indices [I>2σ(I)] | $R_1$ = 0.0411, $wR_2$ = 0.1139 | $R_1$ = 0.0354, $wR_2$ = 0.1025 |
| R indices (all data) | $R_1$ = 0.0444, $wR_2$ = 0.1163 | $R_1$ = 0.0397, $wR_2$ = 0.1061 |

**Table S2** Selected bond lengths (Å) of compound **1.**

| Compound **1** | | | |
|---|---|---|---|
| Mo(1)–Mo(5) | 2.5994(6) | Mo(1)–O(2) | 2.112(3) |
| Mo(1)–O(3) | 1.969(3) | Mo(1)–O(8)#1 | 2.255(3) |
| Mo(1)–O(9) | 2.060(3) | Mo(1)–O(13) | 1.682(4) |
| Mo(1)–O(15) | 1.941(4) | Mo(2)–Mo(4) | 2.5893(6) |
| Mo(2)–O(2) | 2.130(4) | Mo(2)–O(4) | 1.977(3) |
| Mo(2)–O(8)#1 | 2.267(3) | Mo(2)–O(17) | 2.064(4) |
| Mo(2)–O(19) | 1.934(4) | Mo(2)–O(28) | 1.680(4) |
| Mo(3)–Mo(6) | 2.5888(6) | Mo(3)–O(1) | 1.981(3) |
| Mo(3)–O(6) | 2.114(4) | Mo(3)–O(10) | 1.942(4) |
| Mo(3)–O(12)#1 | 2.276(3) | Mo(3)–O(16) | 2.054(4) |
| Mo(3)–O(23) | 1.684(4) | Mo(4)–O(4) | 1.983(3) |

| | | | |
|---|---|---|---|
| Mo(4)–O(6) | 2.097(3) | Mo(4)–O(12)#1 | 2.290(3) |
| Mo(4)–O(18) | 2.065(4) | Mo(4)–O(19) | 1.942(3) |
| Mo(4)–O(26) | 1.687(4) | Mo(5)–O(3) | 1.977(3) |
| Mo(5)–O(5)#1 | 2.283(3) | Mo(5)–O(7) | 2.093(3) |
| Mo(5)–O(15) | 1.943(4) | Mo(5)–O(21) | 2.039(4) |
| Mo(5)–O(25) | 1.683(4) | Mo(6)–O(1) | 1.976(3) |
| Mo(6)–O(5)#1 | 2.298(3) | Mo(6)–O(7) | 2.111(4) |
| Mo(6)–O(10) | 1.939(4) | Mo(6)–O(24) | 2.052(4) |
| Mo(6)–O(30) | 1.679(4) | Mn(1)–O(1) | 2.190(3) |
| Mn(1)–O(1)#2 | 2.190(3) | Mn(1)–O(3) | 2.191(3) |
| Mn(1)–O(3)#2 | 2.191(3) | Mn(1)–O(4) | 2.205(3) |
| Mn(1)–O(4)#2 | 2.205(3) | Mn(2)–O(11)#3 | 2.278(3) |
| Mn(2)–O(14) | 2.131(4) | Mn(2)–O(20) | 2.154(4) |
| Mn(2)–O(27) | 2.193(4) | Mn(2)–O(29)#1 | 2.222(4) |
| Mn(2)–O(31) | 2.279(5) | | |

#1:–x+1,–y+2,–z+2; #2: –x,–y+2,–z+1; #3: –x+1,–y+2,–z+1; #4: –x+1,–y+1,–z+1

**Table S3** Selected angles (°) of compound **1.**

| Compound **1** | | | |
|---|---|---|---|
| O(2)–Mo(1)–Mo(5) | 134.70(10) | O(2)–Mo(1)–O(8)#1 | 73.10(13) |
| O(3)–Mo(1)–Mo(5) | 48.92(10) | O(3)–Mo(1)–O(2) | 86.73(14) |
| O(3)–Mo(1)–O(8)#1 | 81.24(13) | O(3)–Mo(1)–O(9) | 160.13(15) |
| O(8)#1–Mo(1)–Mo(5) | 89.08(8) | O(9)–Mo(1)–Mo(5) | 134.54(11) |
| O(9)–Mo(1)–O(2) | 83.59(14) | O(9)–Mo(1)–O(8)#1 | 79.35(14) |
| O(13)–Mo(1)–Mo(5) | 100.91(13) | O(13)–Mo(1)–O(2) | 96.20(17) |
| O(13)–Mo(1)–O(3) | 101.56(16) | O(13)–Mo(1)–O(8)#1 | 168.87(16) |
| O(13)–Mo(1)–O(9) | 96.73(17) | O(13)–Mo(1)–O(15) | 105.09(17) |
| O(15)–Mo(1)–Mo(5) | 48.03(10) | O(15)–Mo(1)–O(2) | 157.60(15) |
| O(15)–Mo(1)–O(3) | 95.64(14) | O(15)–Mo(1)–O(8)#1 | 85.21(14) |
| O(15)–Mo(1)–O(9) | 87.00(15) | O(2)–Mo(2)–Mo(4) | 134.92(9) |
| O(2)–Mo(2)–O(8)#1 | 72.54(12) | O(4)–Mo(2)–Mo(4) | 49.27(10) |
| O(4)–Mo(2)–O(2) | 86.65(14) | O(4)–Mo(2)–O(8)#1 | 81.62(13) |
| O(4)–Mo(2)–O(17) | 161.27(14) | O(8)#1–Mo(2)–Mo(4) | 89.67(8) |
| O(17)–Mo(2)–Mo(4) | 133.85(11) | O(17)–Mo(2)–O(2) | 84.47(14) |
| O(17)–Mo(2)–O(8)#1 | 79.99(13) | O(19)–Mo(2)–Mo(4) | 48.22(10) |
| O(19)–Mo(2)–O(2) | 156.55(15) | O(19)–Mo(2)–O(4) | 95.97(14) |
| O(19)–Mo(2)–O(8)#1 | 84.75(14) | O(19)–Mo(2)–O(17) | 85.90(15) |
| O(28)–Mo(2)–Mo(4) | 101.05(15) | O(28)–Mo(2)–O(2) | 96.61(18) |
| O(28)–Mo(2)–O(4) | 102.06(17) | O(28)–Mo(2)–O(8)#1 | 168.46(17) |
| O(28)–Mo(2)–O(17) | 95.34(18) | O(28)–Mo(2)–O(19) | 105.56(19) |
| O(1)–Mo(3)–Mo(6) | 49.05(10) | O(1)–Mo(3)–O(6) | 86.87(14) |
| O(1)–Mo(3)–O(12)#1 | 80.87(13) | O(1)–Mo(3)–O(16) | 160.23(15) |
| O(6)–Mo(3)–Mo(6) | 134.97(10) | O(6)–Mo(3)–O(12)#1 | 73.28(13) |

| | | | |
|---|---|---|---|
| O(10)–Mo(3)–Mo(6) | 48.10(11) | O(10)–Mo(3)–O(1) | 95.64(15) |
| O(10)–Mo(3)–O(6) | 156.78(15) | O(10)–Mo(3)–O(12)#1 | 84.30(14) |
| O(10)–Mo(3)–O(16) | 85.72(16) | O(12)#1–Mo(3)–Mo(6) | 88.75(9) |
| O(16)–Mo(3)–Mo(6) | 133.44(11) | O(16)–Mo(3)–O(6) | 84.39(15) |
| O(16)–Mo(3)–O(12)#1 | 79.65(14) | O(23)–Mo(3)–Mo(6) | 100.91(15) |
| O(23)–Mo(3)–O(1) | 101.20(17) | O(23)–Mo(3)–O(6) | 95.81(17) |
| O(23)–Mo(3)–O(10) | 106.27(18) | O(23)–Mo(3)–O(12)#1 | 168.85(17) |
| O(23)–Mo(3)–O(16) | 97.31(18) | O(4)–Mo(4)–Mo(2) | 49.06(10) |
| O(4)–Mo(4)–O(6) | 86.40(14) | O(4)–Mo(4)–O(12)#1 | 81.15(13) |
| O(4)–Mo(4)–O(18) | 159.73(15) | O(6)–Mo(4)–Mo(2) | 134.38(10) |
| O(6)–Mo(4)–O(12)#1 | 73.30(13) | O(12)#1–Mo(4)–Mo(2) | 88.34(9) |
| O(18)–Mo(4)–Mo(2) | 132.91(11) | O(18)–Mo(4)–O(6) | 84.84(14) |
| O(18)–Mo(4)–O(12)#1 | 78.83(15) | O(19)–Mo(4)–Mo(2) | 47.97(11) |
| O(19)–Mo(4)–O(4) | 95.52(14) | O(19)–Mo(4)–O(6) | 156.17(15) |
| O(19)–Mo(4)–O(12)#1 | 83.50(14) | O(19)–Mo(4)–O(18) | 85.39(15) |
| O(26)–Mo(4)–Mo(2) | 100.90(15) | O(26)–Mo(4)–O(4) | 102.22(18) |
| O(26)–Mo(4)–O(6) | 97.52(17) | O(26)–Mo(4)–O(12)#1 | 170.13(17) |
| O(26)–Mo(4)–O(18) | 97.03(19) | O(26)–Mo(4)–O(19) | 105.22(18) |
| O(3)–Mo(5)–Mo(1) | 48.67(10) | O(3)–Mo(5)–O(5)#1 | 81.65(13) |
| O(3)–Mo(5)–O(7) | 86.62(14) | O(3)–Mo(5)–O(21) | 161.28(16) |
| O(5)#1–Mo(5)–Mo(1) | 88.41(8) | O(7)–Mo(5)–Mo(1) | 134.24(10) |
| O(7)–Mo(5)–O(5)#1 | 73.73(13) | O(15)–Mo(5)–Mo(1) | 47.96(10) |
| O(15)–Mo(5)–O(3) | 95.32(14) | O(15)–Mo(5)–O(5)#1 | 83.95(14) |
| O(15)–Mo(5)–O(7) | 157.10(15) | O(15)–Mo(5)–O(21) | 87.00(16) |
| O(21)–Mo(5)–Mo(1) | 134.60(12) | O(21)–Mo(5)–O(5)#1 | 80.12(15) |
| O(21)–Mo(5)–O(7) | 84.22(15) | O(25)–Mo(5)–Mo(1) | 100.69(14) |
| O(25)–Mo(5)–O(3) | 101.54(17) | O(25)–Mo(5)–O(5)#1 | 170.19(16) |
| O(25)–Mo(5)–O(7) | 97.08(17) | O(25)–Mo(5)–O(15) | 104.83(18) |
| O(25)–Mo(5)–O(21) | 95.77(18) | O(1)–Mo(6)–Mo(3) | 49.24(10) |
| O(1)–Mo(6)–O(5)#1 | 81.11(13) | O(1)–Mo(6)–O(7) | 85.80(14) |
| O(1)–Mo(6)–O(24) | 160.05(15) | O(5)#1–Mo(6)–Mo(3) | 88.87(9) |
| O(7)–Mo(6)–Mo(3) | 134.07(10) | O(7)–Mo(6)–O(5)#1 | 73.11(13) |
| O(10)–Mo(6)–Mo(3) | 48.20(11) | O(10)–Mo(6)–O(1) | 95.92(15) |
| O(10)–Mo(6)–O(5)#1 | 84.20(14) | O(10)–Mo(6)–O(7) | 156.73(15) |
| O(10)–Mo(6)–O(24) | 86.21(16) | O(24)–Mo(6)–Mo(3) | 134.01(12) |
| O(24)–Mo(6)–O(5)#1 | 79.37(14) | O(24)–Mo(6)–O(7) | 84.63(15) |
| O(30)–Mo(6)–Mo(3) | 100.04(15) | O(30)–Mo(6)–O(1) | 100.92(18) |
| O(30)–Mo(6)–O(5)#1 | 169.81(18) | O(30)–Mo(6)–O(7) | 96.99(18) |
| O(30)–Mo(6)–O(10) | 105.40(19) | O(30)–Mo(6)–O(24) | 97.60(19) |
| O(1)–Mn(1)–O(1)#2 | 180.0 | O(1)#2–Mn(1)–O(3) | 84.07(13) |
| O(1)–Mn(1)–O(3) | 95.93(13) | O(1)–Mn(1)–O(3)#2 | 84.07(13) |
| O(1)#2–Mn(1)–O(3)#2 | 95.93(13) | O(1)–Mn(1)–O(4)#2 | 84.19(13) |
| O(1)–Mn(1)–O(4) | 95.81(13) | O(1)#2–Mn(1)–O(4) | 84.19(13) |

| | | | |
|---|---|---|---|
| O(1)#2–Mn(1)–O(4)#2 | 95.81(13) | O(3)–Mn(1)–O(3)#2 | 180.0 |
| O(3)–Mn(1)–O(4) | 96.59(12) | O(3)–Mn(1)–O(4)#2 | 83.41(12) |
| O(3)#2–Mn(1)–O(4) | 83.41(12) | O(3)#2–Mn(1)–O(4)#2 | 96.59(12) |
| O(4)#2–Mn(1)–O(4) | 180.0 | O(11)#3–Mn(2)–O(31) | 83.77(17) |
| O(14)–Mn(2)–O(11)#3 | 171.34(15) | O(14)–Mn(2)–O(20) | 87.36(15) |
| O(14)–Mn(2)–O(27) | 96.35(16) | O(14)–Mn(2)–O(29)#1 | 100.98(15) |
| O(14)–Mn(2)–O(31) | 94.61(18) | O(20)–Mn(2)–O(11)#3 | 84.04(14) |
| O(20)–Mn(2)–O(27) | 167.16(16) | O(20)–Mn(2)–O(29)#1 | 101.88(17) |
| O(20)–Mn(2)–O(31) | 85.48(18) | O(27)–Mn(2)–O(11)#3 | 91.86(16) |
| O(27)–Mn(2)–O(29)#1 | 89.51(17) | O(27)–Mn(2)–O(31) | 81.98(18) |
| O(29)#1–Mn(2)O(11)#3 | 81.81(15) | O(29)#1–Mn(2)–O(31) | 162.99(19) |
| Mo(3)–O(1)–Mn(1) | 134.37(17) | Mo(6)–O(1)–Mo(3) | 81.71(13) |
| Mo(6)–O(1)–Mn(1) | 134.73(18) | Mo(1)–O(2)–Mo(2) | 111.75(15) |
| Mo(1)–O(3)–Mo(5) | 82.40(13) | Mo(1)–O(3)–Mn(1) | 134.14(17) |
| Mo(5)–O(3)–Mn(1) | 133.73(17) | Mo(2)–O(4)–Mo(4) | 81.67(12) |
| Mo(2)–O(4)–Mn(1) | 133.49(17) | Mo(4)–O(4)–Mn(1) | 134.29(17) |
| Mo(5)#1–O(5)–Mo(6)#1 | 99.67(13) | Mo(4)–O(6)–Mo(3) | 112.55(16) |
| Mo(5)–O(7)–Mo(6) | 112.76(16) | Mo(1)#1–O(8)–Mo(2)#1 | 101.91(13) |
| Mo(6)–O(10)–Mo(3) | 83.70(14) | Mo(3)#1–O(12)–Mo(4)#1 | 100.13(13) |
| Mo(1)–O(15)–Mo(5) | 84.00(13) | Mo(2)–O(19)–Mo(4) | 83.82(14) |

#1: –x+1, –y+2, –z+2; #2: –x, –y+2, –z+1; #3: –x+1, –y+2, –z+1; #4: –x+1, –y+1, –z+1

**Table S4** Selected bond lengths (Å) of compound **2.**

| Compound **2** | | | |
|---|---|---|---|
| Mo(1)–Mo(3) | 2.5970(5) | Mo(1)–O(2) | 1.937(3) |
| Mo(1)–O(5) | 1.973(3) | Mo(1)–O(7) | 2.126(3) |
| Mo(1)–O(8) | 2.239(3) | Mo(1)–O(18) | 2.056(3) |
| Mo(1)–O(24) | 1.690(3) | Mo(2)–Mo(5) | 2.5907(5) |
| Mo(2)–O(3) | 1.971(3) | Mo(2)–O(7) | 2.136(3) |
| Mo(2)–O(8) | 2.299(3) | Mo(2)–O(13) | 2.038(3) |
| Mo(2)–O(17) | 1.929(3) | Mo(2)–O(23) | 1.681(4) |
| Mo(3)–O(2) | 1.937(3) | Mo(3)–O(5) | 1.976(3) |
| Mo(3)–O(9) | 2.269(3) | Mo(3)–O(10) | 2.106(3) |
| Mo(3)–O(15) | 2.038(4) | Mo(3)–O(27) | 1.680(3) |
| Mo(4)–Mo(6) | 2.5921(5) | Mo(4)–O(1) | 1.943(3) |
| Mo(4)–O(4) | 1.977(3) | Mo(4)–O(6) | 2.099(3) |
| Mo(4)–O(12) | 2.285(3) | Mo(4)–O(14) | 2.032(3) |
| Mo(4)–O(26) | 1.682(3) | Mo(5)–O(3) | 1.976(3) |
| Mo(5)–O(6) | 2.111(3) | Mo(5)–O(12) | 2.299(3) |
| Mo(5)–O(17) | 1.935(3) | Mo(5)–O(21) | 2.054(3) |
| Mo(5)–O(25) | 1.680(4) | Mo(6)–O(1) | 1.938(3) |
| Mo(6)–O(4) | 1.973(3) | Mo(6)–O(9) | 2.282(3) |

| | | | |
|---|---|---|---|
| Mo(6)–O(10) | 2.117(3) | Mo(6)–O(19) | 2.044(4) |
| Mo(6)–O(28) | 1.681(4) | Mn(1)–O(3) | 2.195(3) |
| Mn(1)–O(3)#1 | 2.195(3) | Mn(1)–O(4) | 2.207(3) |
| Mn(1)–O(4)#1 | 2.207(3) | Mn(1)–O(5)#1 | 2.192(3) |
| Mn(1)–O(5) | 2.192(3) | Mn(2)–O(11) | 2.157(3) |
| Mn(2)–O(16)#2 | 2.333(3) | Mn(2)–O(20)#3 | 2.140(3) |
| Mn(2)–O(29) | 2.101(4) | Mn(2)–O(30) | 2.190(4) |
| Mn(2)–O(31) | 2.285(5) | | |

#1:–x+1, –y+2, –z+2; #2: –x, –y+2, –z+1; #3: –x+1, –y+2, –z+1; #4: –x+1, –y+1, –z+1

**Table S5** Selected angles (°) of compound **2.**

| Compound **2** | | | |
|---|---|---|---|
| O(2)–Mo(1)–Mo(3) | 47.91(10) | O(2)–Mo(1)–O(5) | 95.56(13) |
| O(2)–Mo(1)–O(7) | 158.56(13) | O(2)–Mo(1)–O(8) | 85.86(13) |
| O(2)–Mo(1)–O(18) | 86.50(14) | O(5)–Mo(1)–Mo(3) | 48.93(9) |
| O(5)–Mo(1)–O(7) | 86.60(13) | O(5)–Mo(1)–O(8) | 81.02(12) |
| O(5)–Mo(1)–O(18) | 159.89(13) | O(7)–Mo(1)–Mo(3) | 134.70(9) |
| O(7)–Mo(1)–O(8) | 73.38(12) | O(8)–Mo(1)–Mo(3) | 89.23(8) |
| O(18)–Mo(1)–Mo(3) | 133.84(10) | O(18)–Mo(1)–O(7) | 84.44(13) |
| O(18)–Mo(1)–O(8) | 79.18(12) | O(24)–Mo(1)–Mo(3) | 101.11(12) |
| O(24)–Mo(1)–O(2) | 105.37(16) | O(24)–Mo(1)–O(5) | 101.31(15) |
| O(24)–Mo(1)–O(7) | 95.05(15) | O(24)–Mo(1)–O(8) | 168.13(15) |
| O(24)–Mo(1)–O(18) | 97.38(15) | O(3)–Mo(2)–Mo(5) | 49.05(9) |
| O(3)–Mo(2)–O(7) | 86.53(12) | O(3)–Mo(2)–O(8) | 80.45(12) |
| O(3)–Mo(2)–O(13) | 160.20(14) | O(7)–Mo(2)–Mo(5) | 134.49(9) |
| O(7)–Mo(2)–O(8) | 71.97(12) | O(8)–Mo(2)–Mo(5) | 88.87(7) |
| O(13)–Mo(2)–Mo(5) | 135.40(10) | O(13)–Mo(2)–O(7) | 82.77(13) |
| O(13)–Mo(2)–O(8) | 80.41(13) | O(17)–Mo(2)–Mo(5) | 47.98(10) |
| O(17)–Mo(2)–O(3) | 95.33(13) | O(17)–Mo(2)–O(7) | 155.35(14) |
| O(17)–Mo(2)–O(8) | 84.07(13) | O(17)–Mo(2)–O(13) | 87.70(14) |
| O(23)–Mo(2)–Mo(5) | 100.83(13) | O(23)–Mo(2)–O(3) | 102.04(16) |
| O(23)–Mo(2)–O(7) | 97.43(16) | O(23)–Mo(2)–O(8) | 169.06(15) |
| O(23)–Mo(2)–O(13) | 95.85(16) | O(23)–Mo(2)–O(17) | 106.15(17) |
| O(2)–Mo(3)–Mo(1) | 47.89(10) | O(2)–Mo(3)–O(5) | 95.45(13) |
| O(2)–Mo(3)–O(9) | 84.61(13) | O(2)–Mo(3)–O(10) | 157.15(13) |
| O(2)–Mo(3)–O(15) | 87.49(15) | O(5)–Mo(3)–Mo(1) | 48.83(9) |
| O(5)–Mo(3)–O(9) | 81.16(12) | O(5)–Mo(3)–O(10) | 86.79(13) |
| O(5)–Mo(3)–O(15) | 160.99(14) | O(9)–Mo(3)–Mo(1) | 88.38(8) |
| O(10)–Mo(3)–Mo(1) | 134.53(9) | O(10)–Mo(3)–O(9) | 73.25(12) |
| O(15)–Mo(3)–Mo(1) | 134.98(12) | O(15)–Mo(3)–O(9) | 80.43(13) |
| O(15)–Mo(3)–O(10) | 83.43(14) | O(27)–Mo(3)–Mo(1) | 101.28(12) |
| O(27)–Mo(3)–O(2) | 105.35(16) | O(27)–Mo(3)–O(5) | 101.57(16) |

| | | | |
|---|---|---|---|
| O(27)–Mo(3)–O(9) | 169.24(15) | O(27)–Mo(3)–O(10) | 96.41(15) |
| O(27)–Mo(3)–O(15) | 95.70(17) | O(1)–Mo(4)–Mo(6) | 48.00(10) |
| O(1)–Mo(4)–O(4) | 95.52(14) | O(1)–Mo(4)–O(6) | 156.59(13) |
| O(1)–Mo(4)–O(12) | 84.24(13) | O(1)–Mo(4)–O(14) | 85.12(15) |
| O(4)–Mo(4)–Mo(6) | 48.91(9) | O(4)–Mo(4)–O(6) | 87.19(13) |
| O(4)–Mo(4)–O(12) | 80.63(12) | O(4)–Mo(4)–O(14) | 159.76(14) |
| O(6)–Mo(4)–Mo(6) | 135.01(9) | O(6)–Mo(4)–O(12) | 73.23(12) |
| O(12)–Mo(4)–Mo(6) | 88.14(8) | O(14)–Mo(4)–Mo(6) | 132.62(11) |
| O(14)–Mo(4)–O(6) | 84.51(14) | O(14)–Mo(4)–O(12) | 79.30(13) |
| O(26)–Mo(4)–Mo(6) | 100.70(13) | O(26)–Mo(4)–O(1) | 105.64(17) |
| O(26)–Mo(4)–O(4) | 101.05(16) | O(26)–Mo(4)–O(6) | 96.59(16) |
| O(26)–Mo(4)–O(12) | 169.65(16) | O(26)–Mo(4)–O(14) | 98.22(16) |
| O(3)–Mo(5)–Mo(2) | 48.90(9) | O(3)–Mo(5)–O(6) | 86.64(12) |
| O(3)–Mo(5)–O(12) | 80.99(12) | O(3)–Mo(5)–O(21) | 159.18(14) |
| O(6)–Mo(5)–Mo(2) | 134.57(9) | O(6)–Mo(5)–O(12) | 72.73(12) |
| O(12)–Mo(5)–Mo(2) | 89.11(8) | O(17)–Mo(5)–Mo(2) | 47.81(10) |
| O(17)–Mo(5)–O(3) | 95.01(13) | O(17)–Mo(5)–O(6) | 156.02(14) |
| O(17)–Mo(5)–O(12) | 83.87(13) | O(17)–Mo(5)–O(21) | 85.30(14) |
| O(21)–Mo(5)–Mo(2) | 132.69(10) | O(21)–Mo(5)–O(6) | 84.88(13) |
| O(21)–Mo(5)–O(12) | 78.34(13) | O(25)–Mo(5)–Mo(2) | 100.95(13) |
| O(25)–Mo(5)–O(3) | 102.40(16) | O(25)–Mo(5)–O(6) | 96.98(16) |
| O(25)–Mo(5)–O(12) | 169.10(15) | O(25)–Mo(5)–O(17) | 105.97(17) |
| O(25)–Mo(5)–O(21) | 97.49(17) | O(1)–Mo(6)–Mo(4) | 48.19(10) |
| O(1)–Mo(6)–O(4) | 95.84(14) | O(1)–Mo(6)–O(9) | 85.52(13) |
| O(1)–Mo(6)–O(10) | 157.74(14) | O(1)–Mo(6)–O(19) | 85.71(16) |
| O(4)–Mo(6)–Mo(4) | 49.05(9) | O(4)–Mo(6)–O(9) | 80.91(12) |
| O(4)–Mo(6)–O(10) | 85.70(13) | O(4)–Mo(6)–O(19) | 159.61(14) |
| O(9)–Mo(6)–Mo(4) | 89.33(8) | O(10)–Mo(6)–Mo(4) | 133.89(9) |
| O(10)–Mo(6)–O(9) | 72.76(12) | O(19)–Mo(6)–Mo(4) | 133.37(12) |
| O(19)–Mo(6)–O(9) | 78.94(13) | O(19)–Mo(6)–O(10) | 85.40(14) |
| O(28)–Mo(6)–Mo(4) | 101.32(14) | O(28)–Mo(6)–O(1) | 105.24(17) |
| O(28)–Mo(6)–O(4) | 102.26(17) | O(28)–Mo(6)–O(9) | 168.25(16) |
| O(28)–Mo(6)–O(10) | 96.06(16) | O(28)–Mo(6)–O(19) | 96.89(18) |
| O(3)#1–Mn(1)–O(3) | 180.0 | O(3)–Mn(1)–O(4) | 96.61(12) |
| O(3)–Mn(1)–O(4)#1 | 83.39(12) | O(3)#1–Mn(1)–O(4)#1 | 96.60(12) |
| O(3)#1–Mn(1)–O(4) | 83.40(12) | O(4)#1–Mn(1)–O(4) | 180.0 |
| O(5)–Mn(1)–O(3) | 96.76(12) | O(5)#1–Mn(1)–O(3)#1 | 96.76(12) |
| O(5)#1–Mn(1)–O(3) | 83.24(12) | O(5)–Mn(1)–O(3)#1 | 83.24(12) |
| O(5)–Mn(1)–O(4) | 95.77(12) | O(5)–Mn(1)–O(4)#1 | 84.23(12) |
| O(5)#1–Mn(1)–O(4) | 84.23(12) | O(5)#1–Mn(1)–O(4)#1 | 95.77(12) |
| O(5)–Mn(1)–O(5)#1 | 180.0 | O(11)–Mn(2)–O(16)#2 | 171.62(13) |
| O(11)–Mn(2)–O(30) | 94.54(16) | O(11)–Mn(2)–O(31) | 93.67(17) |

| | | | |
|---|---|---|---|
| O(20)#3–Mn(2)–O(11) | 88.70(13) | O(20)#3–Mn(2)–O(16)#2 | 83.74(13) |
| O(20)#3–Mn(2)–O(30) | 165.06(16) | O(20)#3–Mn(2)–O(31) | 84.03(16) |
| O(29)–Mn(2)–O(11) | 99.34(15) | O(29)–Mn(2)–O(16)#2 | 85.71(14) |
| O(29)–Mn(2)–O(20)#3 | 101.22(16) | O(29)–Mn(2)–O(30) | 92.66(18) |
| O(29)–Mn(2)–O(31) | 166.04(18) | O(30)–Mn(2)–O(16)#2 | 91.89(16) |
| O(30)–Mn(2)–O(31) | 81.21(17) | O(31)–Mn(2)–O(16)#2 | 81.99(17) |
| Mo(6)–O(1)–Mo(4) | 83.81(13) | Mo(1)–O(2)–Mo(3) | 84.20(13) |
| Mo(2)–O(3)–Mo(5) | 82.06(12) | Mo(2)–O(3)–Mn(1) | 134.12(16) |
| Mo(5)–O(3)–Mn(1) | 134.00(16) | Mo(4)–O(4)–Mn(1) | 133.36(16) |
| Mo(6)–O(4)–Mo(4) | 82.04(12) | Mo(6)–O(4)–Mn(1) | 134.90(15) |
| Mo(1)–O(5)–Mo(3) | 82.24(12) | Mo(1)–O(5)–Mn(1) | 133.78(16) |
| Mo(3)–O(5)–Mn(1) | 134.05(16) | Mo(4)–O(6)–Mo(5) | 113.15(14) |
| Mo(1)–O(7)–Mo(2) | 111.78(14) | Mo(1)–O(8)–Mo(2) | 102.09(12) |
| Mo(3)–O(9)–Mo(6) | 100.85(12) | Mo(3)–O(10)–Mo(6) | 112.33(14) |
| Mo(4)–O(12)–Mo(5) | 100.11(12) | Mo(2)–O(17)–Mo(5) | 84.21(13) |

#1: –x+1, –y+2, –z+2; #2: –x,–y+2,–z+1; #3: –x+1,–y+2,–z+1; #4: –x+1,–y+1,–z+1

**Table S6** Hydrogen bonding information in compound **1** (Å, °).

| D–H···A | D–H / Å | H···A / Å | D···A / Å | D–H···A / ° |
|---|---|---|---|---|
| 2N(1)–H(1B)···O(22) | 0.89 | 1.90 | 2.787(14) | 173 |

**Table S7** Hydrogen bonding information in compound **2** (Å, °).

| D–H···A | D–H / Å | H···A / Å | D···A / Å | D–H···A / ° |
|---|---|---|---|---|
| 3N(1)–H(1A)···O(22) | 0.89 | 1.85 | 2.730(7) | 169 |
| 3N(1)–H(1C)···O(7) | 0.89 | 2.17 | 3.062(9) | 175 |

**Table S8** Three pairs of (I–I', II–II', III–III') redox peaks involved in electrochemical redox reactions.

| **Redox peaks** | **Electrochemical redox reactions** |
|---|---|
| I–I' | $P_4Mo_6O_{31}^{12-}+2e^-+2H^+ = H_2P_4Mo_6O_{31}^{12-}$ |
| II–II' | $H_2P_4Mo_6O_{31}^{12-}+2e^-+2H^+ = H_4P_4Mo_6O_{31}^{12-}$ |
| III–III' | $H_4P_4Mo_6O_{31}^{12-}+2e^-+2H^+ = H_6P_4Mo_6O_{31}^{12-}$ |

**Table S9** The linear regression equation of compounds **1**–**2** on Cr(VI).

| **Material** | **The linear regression equation** |
|---|---|
| Compound **1** | $I$ (μA) = –0.059 × $C_{(\mu M)}$ – 1.42568 ($R^2$ = 0.996) |
| Compound **2** | $I$ (μA) = –0.078 × $C_{(\mu M)}$ – 0.7245 ($R^2$ = 0.999) |

**Table S10** Comparison of compounds **1**–**2** with reported sensors for the determination of Cr(VI)

| Sensors materials | Method | LOD (μM) | Reference |
|---|---|---|---|
| Compound **1** | i–t | 0.48 | **this work** |
| Compound **2** | i–t | 0.0916 | **this work** |
| Ag GNF | i–t | 0.0125 | S4 |
| $\{Ni(P_4Mo_6)_2\}$ | i–t | 0.321 | S5 |
| Au NPs@Carbon nanotubes | i–t | 0.72 | S6 |
| Ag NPs–carbon SPE | DPV | 0.85 | S7 |
| Au NPs–carbon SPE | | 0.40 | |
| Au NPs @ SPE | DPV | 0.1 | S8 |
| Au NPs @ ITO | CV | 2 | S9 |
| Graphite SPE | LSV | 0.36 | S10 |
| Gold screen printed macro electrode | LSV | 4.4 | S11 |
| Ag plated–GCE | DP–ASV | 0.10 | S12 |

SPE = screen printed electrode; ITO = indium–tin oxide electrode; GNF = golden nanoporous film NPs–nanoparticles; DPV = differential pulse voltammetry; LSV = Linear sweep voltammetry; DP–ASV = differential pulse anodic stripping voltammetry.

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