

Supplementary Material

Electrochemiluminescence immunoassay strategies based on hexagonal Ru-MOF and MoS₂@GO nanosheets: Detection of 5-fluorouracil in serum samples

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Reagents and Apparatus

Polyvinyl pyrrolidone (PVP, $M_w = 40000$) was purchased from Sigma-Aldrich Co., Ltd (C). Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$, 99%) was bought from Sinopharm Chemical Reagent Co., Ltd. sulfuric acid (H_2SO_4 , 95%~98%) was obtained from Chinasun Specialty Products Co.,Ltd. Pyrazine ($C_4H_4N_4$, 99%) was purchased from Macklin (Shanghai) Co., Ltd. Thiourea (CH_4N_2 , 99%) was bought from Tokyo Chemical Industry. Potassium peroxodisulfate ($K_2S_2O_8$, 99%) was obtained from Sinopharm Chemical Reagent Co., Ltd. Tris(4,4'-dicarboxylicacid-2,2'-bipyridyl)ruthenium(II) dichloride($Ru(dcbpy)_3^{2+}$), 98%) was purchased from Shanghai yuanye Bio-Technology Co., Ltd. Ethyl-3-(dimethyl aminopropyl) carbodiimide (EDC, 98%) and N-hydroxysuccinimide (NHS, 97%) were bought from J&K Scientific (Beijing, China). Graphite powder was purchased from Sinopharm Chemical Reagent Co., Ltd. Phosphorus pentoxide(P_2O_5 , 98%) was bought from Sinopharm Chemical Reagent Co., Ltd. Hexaammonium Molybdate ($(NH_4)_6Mo_7O_{24}$, 98%) was purchased Shanghai Adamas Reagent Co., Ltd. Potassium permanganate($KMnO_4$, 99.5%) was obtained from Sinopharm Chemical Reagent Co., Ltd. 5-FU coating antigen and 5-FU antibody were obtained from our group. Bovine serum albumin (BSA) was acquired from Sigma-Aldrich Co., Ltd (Shanghai). All other reagents and materials were commercially available and of analytical reagent grade.

The ECL emission was measured by an MPI-A ECL analytical system (Xi'An Remex Electronic Science & Technology Co., Ltd, Xi'An, China) in ECL buffer solution. The potential scan was from -1.6 V to 0 V with the voltage of the photomultiplier tube (PMT) set at 700 V. A three-electrode system was used in the experiment, including the modified glassy carbon electrode as working electrode (GCE, $\Phi = 3$ mm), a platinum wire counter electrode and an Ag/AgCl reference electrode

(saturated KCl solution). The Scanning Electronic Microscopy (SEM) was supplied by Hitachi SU8010 SEM (Hitachi Co., Japan). The Transmission Electron Microscope (TEM) images were obtained from Tecnai G2 F20 S-TWIN 200KV (FEG, FEI Co., USA). UV-vis absorption spectrum was recorded with Agilent 8453 UV-vis spectrophotometer (Agilent Co., America). EIS was undertaken using an RST electrochemical workstation (Suzhou Risetest Instrument Co., Ltd, Suzhou, China). ECL emission spectrum of Ru-MOF was carried out with the RFAS-1 automatic electrochemiluminescence spectrophotometer (Xi'An Remex Electronic Science & Technology Co., Ltd, Xi'An, China), using the same three-electrode system as that in the ECL detection.

Buffer solution

Phosphate-buffered saline stock solution (PBS, 0.1 mol L⁻¹) was prepared by KCl (0.1 mol L⁻¹), NaCl (0.1 mol L⁻¹), Na₂HPO₄ (6.4 mmol L⁻¹) and KH₂PO₄ (1.0 mmol L⁻¹). K₂S₂O₈ solution (0.1 mol L⁻¹) was used as ECL detection buffer solution. Fe(CN)₆³⁻/Fe(CN)₆⁴⁻ standard solution containing KCl (0.1 mol L⁻¹), Fe(CN)₆³⁻ (5 mmol L⁻¹) and Fe(CN)₆⁴⁻ (5 mmol L⁻¹) was employed to measure electrochemical impedance spectroscopy (EIS).

Table S1**Table S1.** Properties of comparable methods for determination of 5-FU

Methods	LODs (ng mL ⁻¹)	Analytical ranges (ng mL ⁻¹)	References
HPLC	2.0	5~500	1
GC-MS	0.167	0.5~50	2
GC-MS/MS	40	0.09~4	3
EC Sensor	34.7	104~6×10 ⁵	4
Fluorescence	6.8	1.32~1320	5
ECLIA	3.1×10 ⁻⁵	0.0001~100	This work

Table S2**Table S2** Selectivity of the ECL immunosensor to 11 interfering substances

Interferences	Cross-interference rate (%)
5-fluorouracil	100
Carmofur	5.1
5-fluoro-2'-deoxyuridine	9.9
Gimeracil	< 0.10
Capecitabine	< 0.10
5-bromouracil	< 0.10
Uridine	< 0.10
5-Bromo-2'-deoxyuridine	< 0.10
Uracil	< 0.10
Cytosine	< 0.10
Thymine	< 0.10
5-fluoro-1, 3-dimethylpyrimidine	< 0.10

References

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