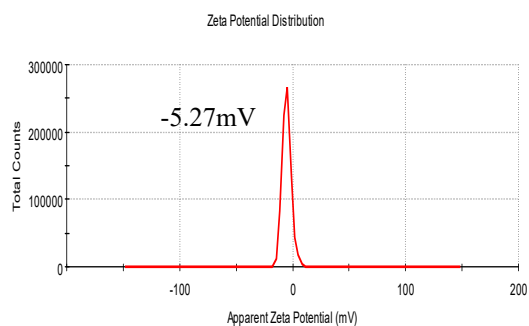


# Rapid and selective RRS determination of ferrocyanide with nanogold surface molecularly imprinted polymethacrylic acid probe

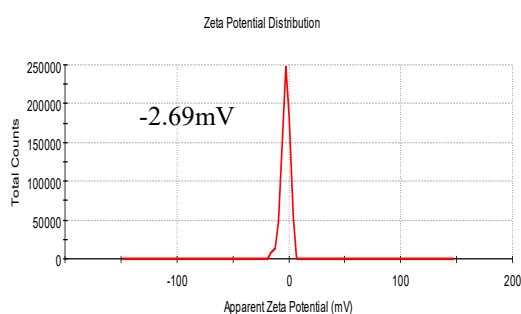
Yumei Li <sup>a,b,c</sup>, Yue Liu <sup>a,b,c</sup>, Aihui Liang <sup>a,b,c\*</sup>, Zhiliang Jiang <sup>a,b,c\*</sup>

<sup>a</sup> Key Laboratory of Ecology of Rare and Endangered Species and Environmental Protection (Guangxi Normal University), Ministry of Education, Guilin 541004, China; <sup>b</sup> Guangxi Key Laboratory of Environmental Pollution Control Theory and Technology, Guilin 541004, China; <sup>c</sup> Guangxi Key Laboratory of Environmental Processes and Remediation in Ecologically Fragile Regions.

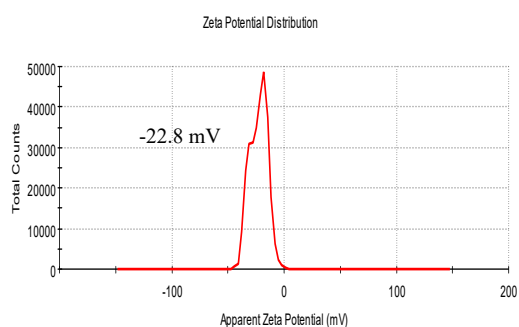
A



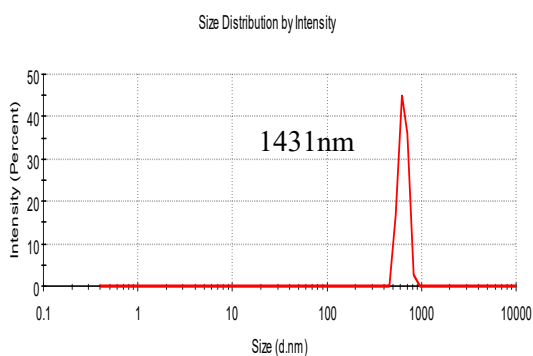
B



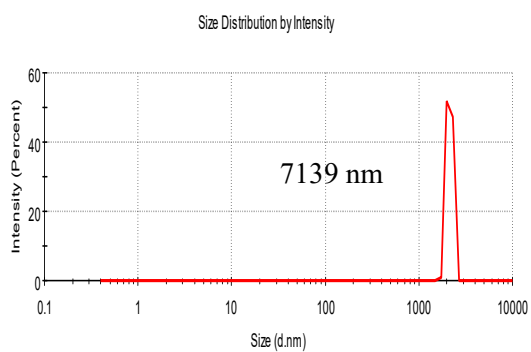
C



D



E



F

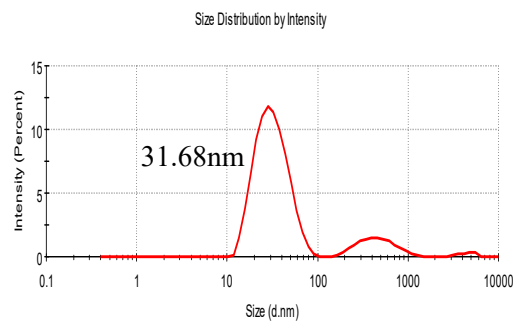
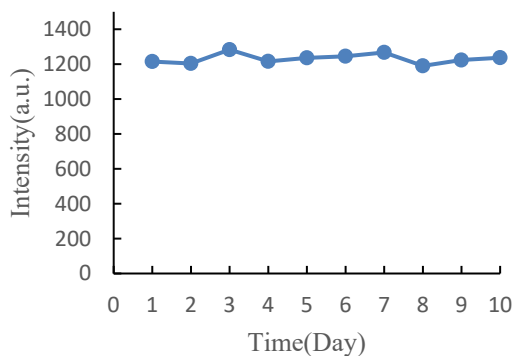


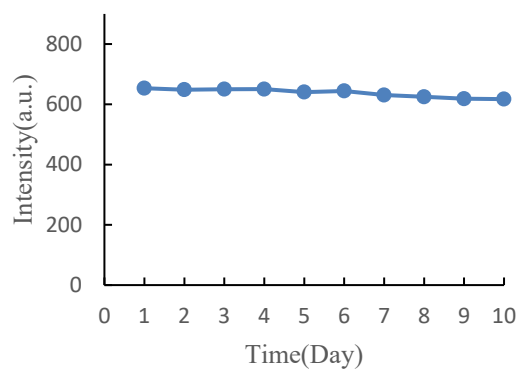
Fig. S1 Zeta potential and particle size distribution of AuNP@MIP, AuNP, and MIP

A: Zate potential diagram of 0.2 g/L AuNP@MIP; B: Zate potential diagram of 0.2 g/L MIP; C: Zate potential diagram of AuNP; D: Particle size diagram of 0.2 g/L AuNP@MIP; E: Particle size chart of 0.2 g/L MIP; F: Particle size chart of AuNP

A



B



C

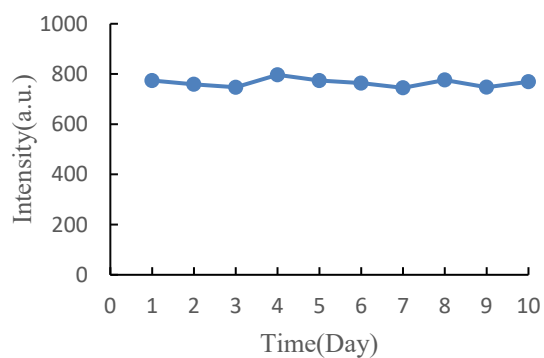


Fig. S2 Stability of AuNP@MIP, AuNP, and MIP over time

A: RRS signal variation of AuNP@MIP over time; B: RRS signal variation of AuNP over time; C: RRS signal variation of AuNP over time.

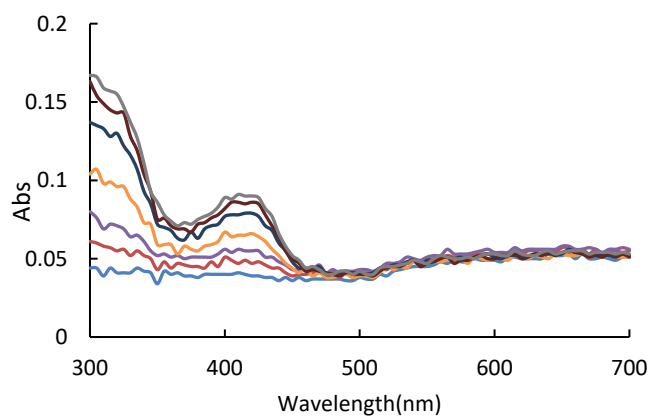
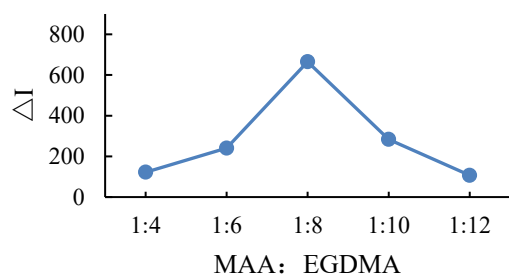


Fig. S3 Absorption spectrum of AuNP@MIP -  $K_4Fe(CN)_6$  - HCl system

AuNP<sub>10nm</sub>@MIP (0.04 g/L) + HCl (0.004 mol/L) +  $K_4Fe(CN)_6$  (0,25,50,125,175,200,250  $\mu$ mol/L).

A



B

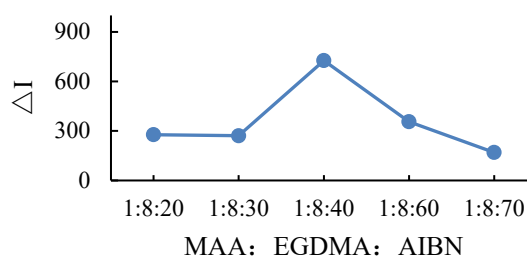
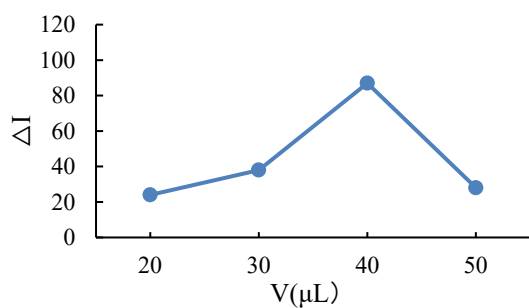


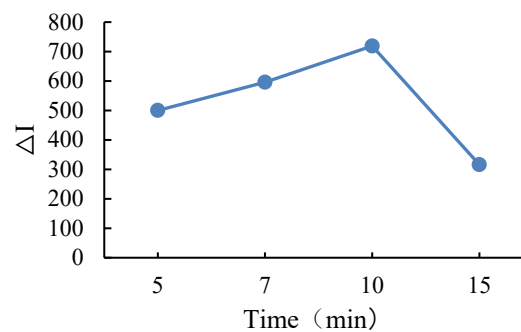
Fig. S4 Optimization of AuNP@MIP preparation conditions

A: Effect of functional monomer MAA:  $K_4Fe(CN)_6$  (0.25 mmol) + EGDMA (10 mmol) + 24.2 mg AIBN + 70 °C + 2 h + MAA (1, 1.5, 2, 2.5, 3 mmol); B: Effect of cross-linker EGDMA:  $K_4Fe(CN)_6$  (0.25 mmol) + MAA (2 mmol) + 24.2 mg AIBN + 70 °C + 2 h + EGDMA (5, 7.5, 10, 15, 17.5 mmol);

C



D



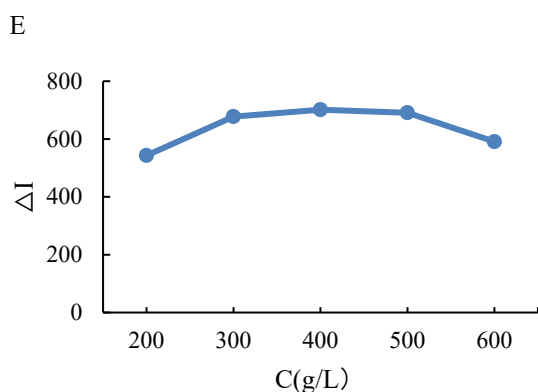


Fig. S5 the Optimization of AuNP @MIP-K<sub>4</sub>Fe(CN)<sub>6</sub>-HCl analysis system conditions

C: Effect of HCl concentration: AuNP<sub>10nm</sub>@MIP (0.04 g/L) + K<sub>4</sub>Fe(CN)<sub>6</sub> (10 μmol/L) + 0.2 mol/L HCl (20, 30, 40, 50 μL); D: Effect of reaction time: AuNP<sub>10nm</sub>@MIP (0.04 g/L) + K<sub>4</sub>Fe(CN)<sub>6</sub> (10 μmol/L) + HCl (0.004 mol/L) + reaction time (5 min, 7 min, 10 min, 15 min); E: Effect of AuNP@MIP concentration: K<sub>4</sub>Fe(CN)<sub>6</sub> (10 μmol/L) + HCl (0.004 mol/L) + 0.2 g/L AuNP<sub>10nm</sub>@MIP (200 μL, 300 μL, 400 μL, 500 μL, 600 μL)

Table. S1 Comparison of analytical methods for the determination of potassium ferricyanide

Determination method	Principle	Linear range(μmol/L)	Comments	Ref.
Fluorescent	A novel fluorescent Si QDs probe for the rapid detection of potassium K <sub>4</sub> Fe(CN) <sub>6</sub> was introduced.	0.05~8 μg/mL	Selective but complicated operation.	[18]
RRS	A simple and rapid RRS method was developed for the detection of potassium K <sub>4</sub> Fe(CN) <sub>6</sub> in table salt.	0.03~5.7 μg/mL	The detection method is sensitive and has a low linear range.	[22]
Electrochemistry	A prototype of a current-limiting sensor was established to detect K <sub>4</sub> Fe(CN) <sub>6</sub> and improve the reaction efficiency through the high surface area of the porous Ni electrode.	3~1000	The detection method is novel, but the detection range is too high.	[23]
Voltammetry	Cyclic voltammetry was used to detect K <sub>4</sub> Fe(CN) <sub>6</sub> .	1000~3000	Good reproducibility and accuracy, but more reagent types required.	[24]
Au@MIP RRS	In this paper, the detection of K <sub>4</sub> Fe(CN) <sub>6</sub> by nanosurface molecularly imprinted	0.02~0.4	The detection method is simple, sensitive, fast, with low	This work

polymer spectral probes with selective recognition using RRS detection method is introduced.

detection linear range and low detection limit.

Table. S2 Effect of interfering ions on the RRS system

interfering ions	Relative multiple	Relative error (%)	interfering ions	Relative multiple	Relative error (%)
Ni <sup>2+</sup>	1000	-4.9%	Ba <sup>2+</sup>	1000	+0.4%
Co <sup>2+</sup>	1000	-1.2%	Zn <sup>2+</sup>	1000	+6.7%
Mn <sup>2+</sup>	1000	-8.2%	K <sup>+</sup>	1000	-1.6%
Mg <sup>2+</sup>	1000	+5.2%	Al <sup>3+</sup>	1000	-5.6%
Ca <sup>2+</sup>	1000	+0.1%	Cd <sup>2+</sup>	1000	-2.4%
PO <sub>4</sub> <sup>3-</sup>	1000	+7.3%	(NH <sub>4</sub> ) <sub>2</sub> MoO <sub>4</sub> O <sub>13</sub>	1000	-3.7%
K <sub>3</sub> Fe(CN) <sub>6</sub>	1000	-1.9%	KSCN	1000	+1.9%

Table. S3 Sample measurement results

Sample	Average (μmol/L)	Added (μmol/L)	Detected (μmol/L)	Recovery (%)	RSD (%)	Content (mg/kg)
1	0.3510	0.05	0.3964	90.8	2.38	2.96
2	0.3224	0.05	0.3680	91.2	2.41	2.72
3	0.2897	0.05	0.3360	92.6	1.50	2.44
4	0.3025	0.05	0.3483	91.6	3.02	2.55
5	0.2826	0.05	0.3297	94.2	2.17	2.38
6	0.2735	0.05	0.3194	91.8	1.08	2.30