Strong nanocatalysis of silver-doped carbon nitride and its application to aptameric SERS and RRS coupled dual-mode detection of ultra-trace K⁺

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1



Figure S1 Particle size distribution of KCl-Apt- AgCNs-GL- HAuCl_ systems.

A. 0.1 μmol/L Apt +7.2 μg/mL CNs +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB. B. 0.1 μmol/L Apt +7.2 μg/mL CNs +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB +50 nmol/L KCl. C. 0.1 μmol/L Apt +7.2 μg/mL CNs +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB +100 nmol/L KCl.



Figure S2. Scanning transmission electron microscope (STEM) and EDS mapping.

A. STEM of AgCNs. B. Ag EDS mapping in AgCNs. C. STEM of reaction system. D. Au EDS mapping in reaction system.



Figure S3. Optimization of analysis conditions.

A. Optimization of reaction temperature. 0.1 μmol/L Apt +7.2 μg/mL AgCNs +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB. B. Optimization of reaction time. 0.1 μmol/L Apt +7.2 μg/mL AgCNs +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB. C. Optimization of AgCNs concentration. 0.1 μmol/L Apt +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB. D. Optimization of Apt concentration. 7.2 μg/mL AgCNs +5 mmol/L GL +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB. E. Optimization of HAuCl₄ concentration. 0.1 μmol/L Apt +7.2 μg/mL AgCNs +5 mmol/L GL +1.25 mmol/L HAuCl₄ +1 μmoL/L VBB. E. Optimization of HAuCl₄ concentration. 0.1 μmol/L Apt +7.2 μg/mL AgCNs +5 mmol/L GL +1.25 mmol/L HAuCl₄ +1 μmoL/L VBB. F. Optimization of GL concentration. 0.1 μmol/L Apt +7.2 μg/mL AgCNs +0.25 mmol/L HAuCl₄ +1 μmoL/L VBB. G. Optimization of VBB concentration. 0.1 μmol/L Apt +7.2 μg/mL AgCNs +5 mmol/L GL +0.25 mmol/L HAuCl₄.



Figure S4. The pure VBB Raman spectrum.



Figure S5. Peak area fitting.



Figure S6. SERS, RRS and dual-mode working curves.



Figure S7. Influence of coexisting substances.

Table S1. Precision of SERS, RRS and dual-mode Apt-mediated nanocatalytic system.

| Method | K+ concentration (nmol/L) | Single measured value (A.U.) | Average (A.U.) | RSD (%) |
|----------|---------------------------------|---------------------------------------|-------------------|------------|
| SERS | 20 | 476, 483, 551, 582, 495, 449, 465 | 500.14 | 9.67 |
| | 40 | 841, 838, 912, 793, 813, 799, 841 | 833.86 | 4.78 |
| RRS | 20 | 135, 128, 128, 129, 119, 127, 131 | 128.14 | 3.78 |
| | 40 | 178, 186, 184, 179, 183, 181, 177 | 181.14 | 1.84 |
| SERS_RRS | 20 | 611, 611, 679, 711, 614, 576, 596 | 628.1 | 7.68 |
| JENJ-NNJ | 40 | 1019, 1024, 1096, 972, 996, 980, 1018 | 1014.9 | 4.04 |

Table S2. Comparison of reported Apt methods for determining potassium ions.

| Method | Method principle | LR | LOD | Comments | Ref. |
|--|---|----------------------------|-----------------|---|-----------------|
| Colorimetric | Based on DNA G-quadruplex conformation and salt-induced AuNPs aggregation. | 1 µM -1 mM | 0.42 μmol/L | Low sensitivity | 37 |
| Fluorescence | Two arm fragments and a dual- labeled Apt serving as a signal transduction probe complementary of arm fragment sequence. | 0.05-1.4 mmol/L | 0.014 mmol/L | Narrow linear range | 38 |
| Fluorescence | HPPA can be oxidized by H_2O_2 into a fluorescent product in the presence of DNAzyme. | 2.5 μM -5 mM(logarithm) | - | Complex material preparation | 39 |
| Electrochemical | Based on a conformational change to afford an electric signal transduced electrochemically. | 3.61–4.85 mM | - | Narrow linear range | 47 |
| Fluorescence resonance energy transfer | Cationic conjugated polyelectrolytes- triggered conformational change of molecular beacon Apt. | - | 1.5nM | High sensitivity | 48 |
| SER-RRS dual- mode | Apt reduce the SERS and RRS signal of CNs. After adding K ⁺ , the signals recovery. | 5-150 nmol/L | 0.92 nmol/L | Simple, fast, and highly sensitive. | This article |

Table S3. Water sample analysis results (n=5) .

| Samples | measured value (nmol/L) | average value (nmol/L) | spiked sample (nmol/L) | spiked sample measured (nmol/L) | Recovery rate (%) | RSD (%) | K ⁺ actual value (nmol/L) |
|----------|--------------------------------------|------------------------------|-------------------------------|--|-------------------------|------------|--|
| Sample 1 | 7.75, 7.94, 8.04, 8.11, 8.12 | 7.99 | 50 | 59.50 | 103.02 | 1.92 | 15.98 |
| Sample2 | 31.54, 30.21, 31.18, 31.07, 32.01 | 31.20 | 50 | 79.91 | 97.42 | 2.13 | 62.40 |
| Sample 3 | 17.22, 17.17, 17.68, 17.35, 16.81 | 17.25 | 50 | 67.35 | 100.21 | 1.82 | 35.50 |