Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

Highly sensitive surface-enhanced Raman scattering detection of adenosine triphosphate based on core-satellite nanoassemblies

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Experimental details

SERS comparison of various silver-coated AuNS samples. A 1 mL aliquot of the washed 50 or 60 nm AuNS solution (0.2 nM) was transferred to a 1.5 mL centrifuge tube. After each subsequent chemical addition, the sample was briefly vortexed. A small volume (varied between 0 and 10 μL) of $AgNO_3$ (0.1 M) and an equivalent volume of AA (0.1 M) were added to each solution. The reduction of $AgNO_3$ by AA was initiated by the addition of NH_4OH (2 μL, 29%), and the color of the solution began to darken. About 5 min later, the solution color was stable, indicating that the reaction was complete. The silver-coated AuNS samples were then labeled with dye by adding 10 μM final concentration of 4-MBA (dissolved in ethanol) to the solution, and allowing it to incubate for 4 h. The solution was centrifuged at 1000 g for 15 min. Then the supernatant was removed to give a residual volume of 10 μL. Then, 10 μL of the residual solution was deposited on a cleaned silica slide for further SERS measurement.

Calculation of limit of detection (LOD)

To investigate The LOD was estimated without ATP giving SERS signal at least three times higher than background. The standard curve of ATP was plotted as:

$$Y = A + BX \quad \text{(S-1)}$$

Where A and B are the intercept and slope, respectively, obtained via linear regression for the signal concentration curve for variable Y representing the SERS signal at log ATP concentration of X (pM). In this study, A is 6496.18 and B is 528.25, respectively.

At the LOD,

$$Y = Y_{blank} + 3SD \quad \text{(S-2)}$$

where Y_{blank} is the SERS signal of the blank (without ATP), and SD is the standard deviation of the blank.

The LOD is calculated as $$\text{LOD (in log units)} = \frac{(Y_{blank} + 3SD) - A}{B} \quad \text{(S-3)}$$

Theoretically, Y_{blank} should equal the intercept (no ATP present). Thus,

$$\text{LOD (in log units)} = \frac{3SD}{B} \quad \text{(S-4)}$$

Supporting figures and tables

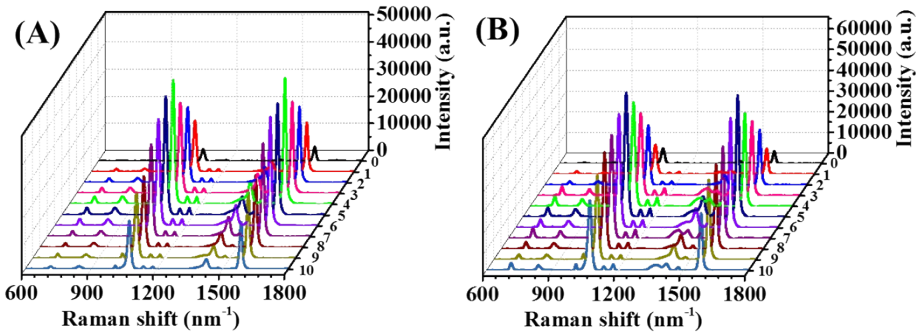

Fig. S1 SERS spectra of AuNS@Ag samples (various amounts of silver coating) prepared with different AuNSs. (A) 50 nm AuNS; (B) 60 nm AuNS. SERS detection parameters: $\lambda_{excitation}$ = 785 nm, accumulation time = 10 s, laser power = 50 mW.

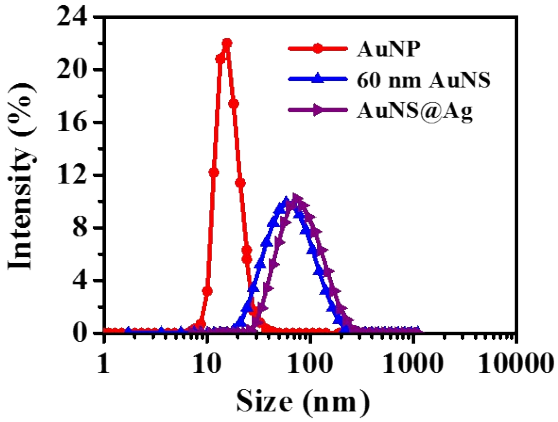

Fig. S2 DLS characterization of the preparation of AuNS@Ag (using 13 nm AuNP as a seed) at different stages with different sizes.

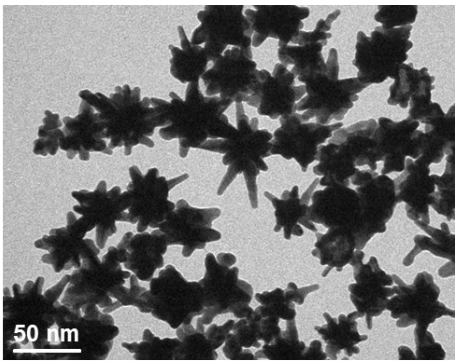

Fig. S3 The TEM image of 60 nm AuNS.

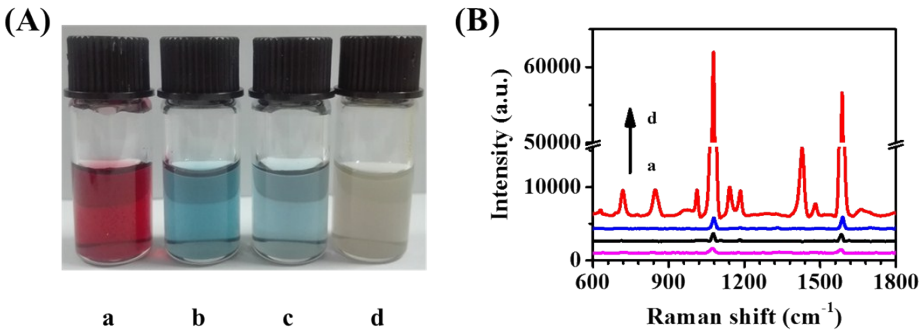

Fig. S4 (A) The photographic images corresponding to (a) AuNP, (b) 50 nm AuNS, (c) 60 nm AuNS, (d) AuNS@Ag. (B) SERS spectra corresponding to (a) AuNP, (b) 50 nm AuNS, (c) 60 nm AuNS, (d) AuNS@Ag.

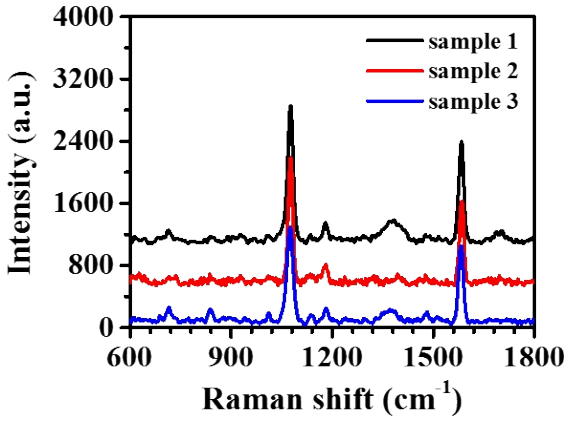

Fig. S5 SERS spectra of 4-MBA for quantitative evaluation of the ATP in 20% human serum samples. SERS detection parameters: $\lambda_{excitation}$ = 785 nm, accumulation time = 10 s, laser power = 100 mW.

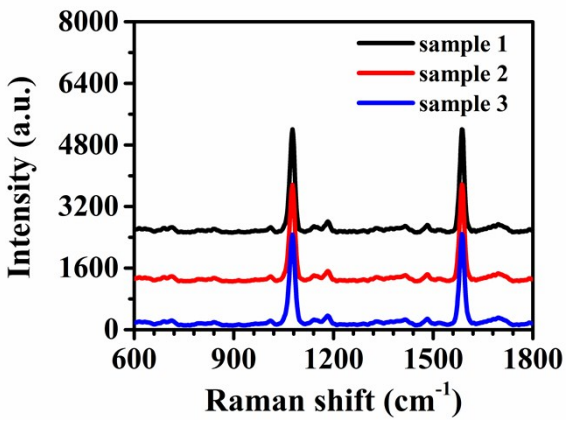

Fig. S6 SERS spectra of 4-MBA for quantitative evaluation of the ATP in diluted human urine samples. SERS detection parameters: $\lambda_{excitation}$ = 785 nm, accumulation time = 10 s, laser power = 100 mW.

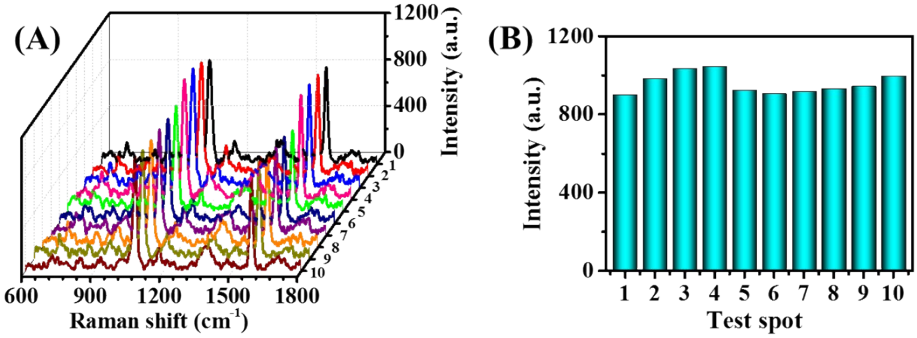

Fig. S7 (A) Reproducibility of the SERS spectra of 4-MBA collected at 10 randomly selected spots on the substrate (50 pM ATP). (B) Signal intensity of the 1078 cm^{-1} line from 4-MBA collected at 10 randomly selected spots on the substrate (50 pM ATP). SERS detection parameters: $\lambda_{excitation}$ = 785 nm, accumulation time = 10 s, laser power = 100 mW.

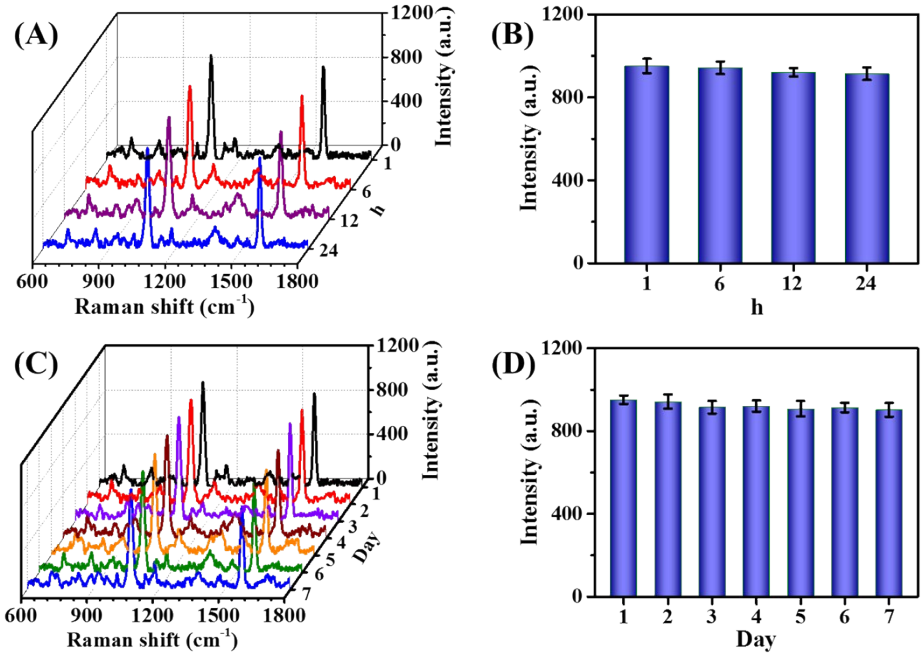

Fig. S8 Stability of the SERS spectra of 4-MBA within 24 h (A) and 7 days (C) (50 pM ATP). Signal intensity of the 1078 cm^{-1} line from 4-MBA within 24 h (B) and 7 days (D). SERS detection parameters: $\lambda_{excitation}$ = 785 nm, accumulation time = 10 s, laser power = 100 mW.

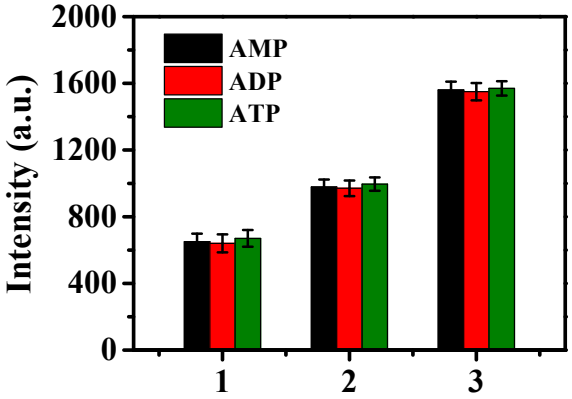

Fig. S9 Histograms of the selectivity of the sensor examined by being incubated in the following samples under the same experimental conditions: AMP, ADP and ATP; three concentrations (**1**: 10 pM; **2**: 50 pM; **3**: 500 pM) were used for the determination. The SERS intensity of the 1078 cm^{-1} peak was utilized for comparison. SERS detection parameters: $\lambda_{excitation}$ = 785 nm, accumulation time = 10 s, laser power = 100 mW.

Table S1. Comparison of different methods for the detection of ATP

Detection method	Linear range	LOD	Ref.
SERS	1 pM~1 nM	0.5 pM	This work
Fluorescence	10~800 nM	4.5 nM	1
Colorimetry	0.05~10 μM	10 nM	2
Chemiluminescnce	0.1~2.5 nM	0.03 nM	3
Electrochemistry	0.1 pM~100 nM	30 fM	4
qPCR	50 nM~5 mM	17 nM	5
Photoelectrochemistry	0.5 pM~5 nM	0.18 pM	6

Table S2. Recovery test for ATP detection in 20% human serum samples using our method and ATP bioluminescent assay kit

Sample	Spiked concentration (pM)	Detected concentration by this method (pM)	Recovery (%)	Detected concentration by ATP kit (pM)	Recovery (%)
1	1000	982.38 ± 7.39	98.2	995.34 ± 2.09	99.5
2	500	494.78 ± 5.09	99.0	498.44 ± 2.53	99.7
3	100	88.75 ± 7.30	88.8	96.01 ± 1.08	96.0

Table S3. Biological sample test for ATP in diluted human serum using our method and ATP bioluminescent assay kit

Sample	Detected concentration by this method (nM)	Detected concentration by ATP kit (nM)
1	0.98	0.73
2	0.93	0.80
3	0.86	0.78

References

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