Supporting Information

A Surface-Enhancement Raman Scattering Sensing Strategy for Discriminating Trace Mercuric Ion (II) from Real Water Samples in Sensitive, Specific, Recyclable and Reproducible Manners

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Enhancement factor (EF) calculation. In detail, the EF value was calculated using the following well-established equation[1-2]:

$$EF = \frac{I_{SERS} \times N_{bulk}}{I_{bulk} \times N_{SERS}} \quad \text{(S-1)}$$

Whereas, I_{SERS} and I_{bulk} are the intensity of the same Raman band for the SERS and bulk Raman spectra, respectively. N_{bulk} is the number of bulk molecules probed in a bulk sample, and N_{SERS} is the number of molecules adsorbed on the SERS active substrate. Thus, for SERS examination, a certain volume V_{SERS} of R6G aqueous solution was dispersed on an area of S_{SERS} at a concentration of C_{SERS} on the AuNPs@SiNWAr substrate. In contrast, a certain volume V_{bulk} of R6G aqueous solution was dispersed on an area of S_{bulk} at a concentration of C_{bulk} on the SiNWAr substrate. Both the substrates were dried in air. Foregoing equation thus comes:

$$EF = \frac{I_{SERS}}{I_{bulk}} \times \frac{S_{SERS} \times V_{bulk} \times C_{bulk}}{S_{bulk} \times V_{SERS} \times C_{SERS}} \quad \text{(S-2)}$$

For objective calculation, Raman measurements were conducted under identical experimental conditions (laser wavelength, laser power, microscope objective/lenses, spectrometer, etc.).

Calculation of limit of detection (LOD). The LOD was estimated without Hg^{2+} ions giving SERS signal at least three times higher than background (DI water).[3] The standard curve of Hg^{2+} ions was plotted as

$$Y = A + B \times Log_{10}X \quad \text{(S-3)}$$

where, A and B are the variable obtained via least-square root linear regression for the signal-concentration curve and variable Y represents the normalized SERS signal ($I_{withHg^{2+}} / I_{BG}$) at Hg^{2+} concentration of X ($C_{Hg^{2+}}$).

When $Y = Y_{blank} + 3SD$ (S-4)

where, SD is the standard deviation and Y_{blank} is the SERS signal of blank sample (DI water).

The LOD was calculated as $LOD = 10^{[(Y_{\text{blank}} + 3SD)/Y_{\text{blank}} - A]/\text{B}]}$ (S-5)

SD was calculated according to the well-known formula:

$$SD = \sqrt{\frac{1}{n-1} \times \sum_{i=1}^{n} (X_i - X_{average})^2} \quad \text{(S-6)}$$

where, n is the total number of the Hg^{2+} ions standard sample. X_i is the "i" sample of the series of measurements. $X_{average}$ is the average value of the SERS signals obtained for the specific series of identical samples repeated n times.

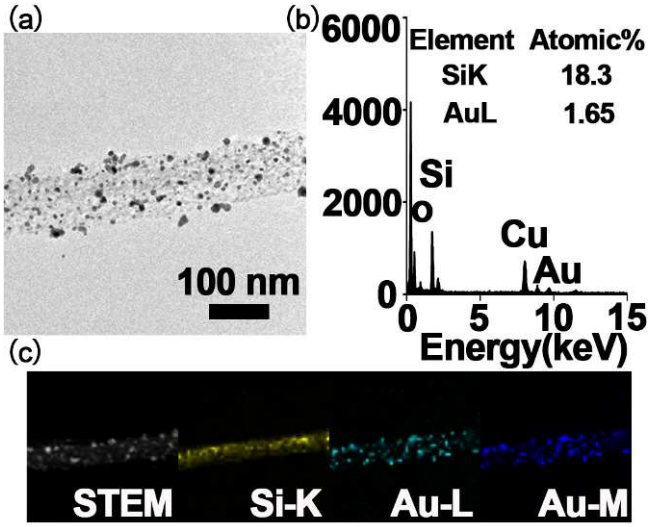

Figure S1. (a) TEM image of a single AuNPs@SiNW, (b) the elemental composition of the AuNPs@SiNW determined by energy-dispersive X-ray spectroscopy (EDS) and (c) its elemental mapping in the high-angle annular dark-field scanning TEM (HAADF-STEM). Inset in (b) represents the corresponding elemental ratio calculated by the EDS software. The TEM image shows a large amount of AuNPs with average sizes of 20 nm are uniformly decorated on the surface of the single SiNW. The EDX pattern indicates that the resultant AuNPs@SiNW contains Si and Au of 18.3 and 1.65% Atomic concentration, respectively, providing additional demonstration of the existence of Si and Au in the substrate. In addition, Si-K, Au-L, and Au-M are detectable in the HAADF-STEM image, further suggesting Si and Au elements are uniformly distributed in the AuNPs@SiNW.

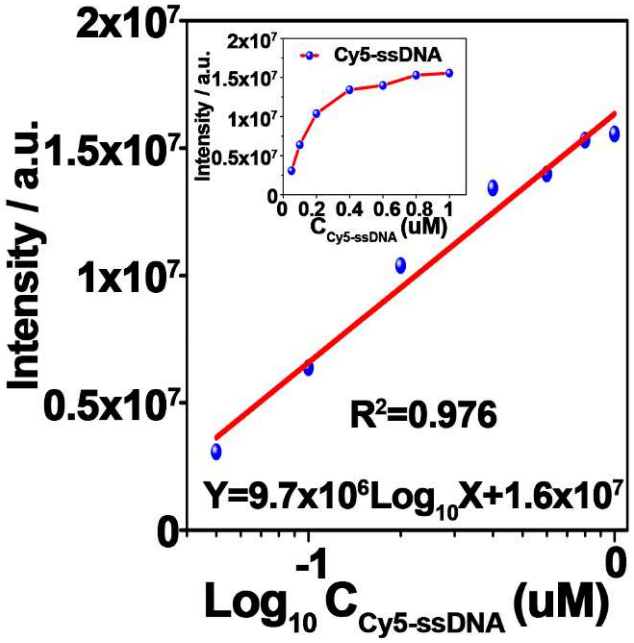

Figure S2 . The linear fitting between the fluorescence intensity and logarithmic concentration of Cy5-ssDNA. The regression equation is $Y = 9.7\times10^{6} Log_{10}X + 1.6\times10^{7}$ with a correlation coefficient of 0.976, where Y represents fluorescence intensity and X represents $C_{Cy5-ssDNA}$, respectively. Inset presents the calibration curve of fluorescence intensity versus Cy5-ssDNA at different concentrations. According to the linear regression equation, it is readily calculated that ~17 strands of Cy5-ssDNA are linked on the surface of one Au NP in AuNPs@SiNWAr

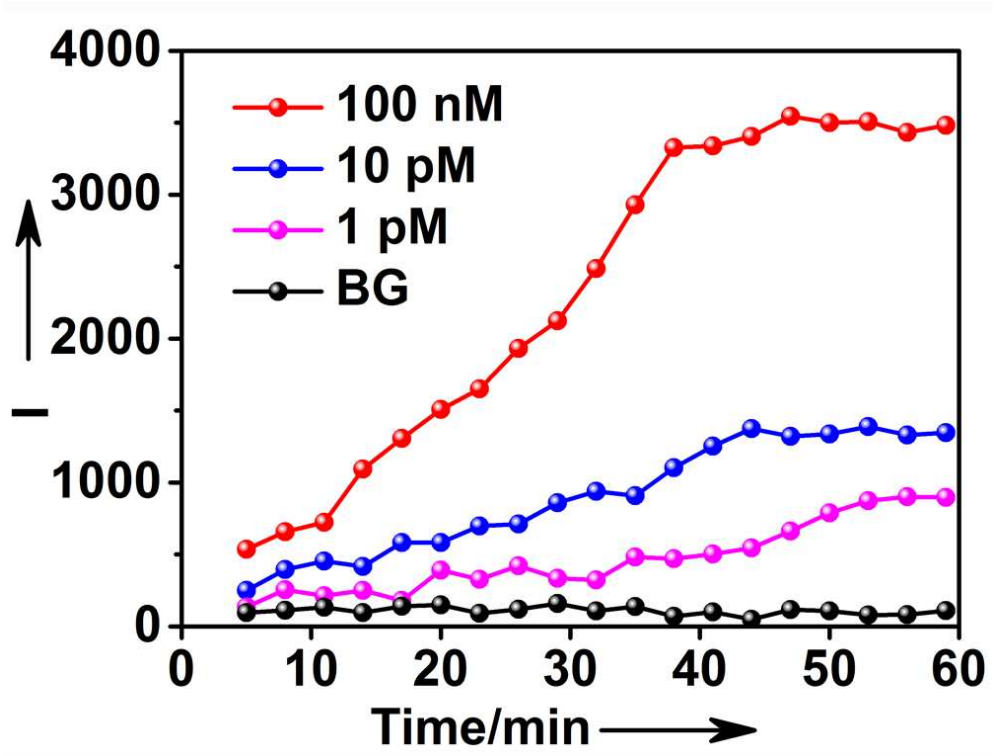

Figure S3. Kinetic studies of the developed SERS sensor at different Hg^{2+} concentrations of 0 (BG), 1 pM, 10 pM and 100 nM. Raman intensities of Cy5 1366 cm^{-1} band are collected at the interval of 3 min. As shown in the Figure, the steady-state of reaction arrives at 35 min, 45 min and 55 min when Hg^{2+} concentration is 100 nM, 10 pM and 1 pM, respectively, indicating such kinetic property is also dependent on Hg^{2+} concentration, which is consistent with previous report.[4]

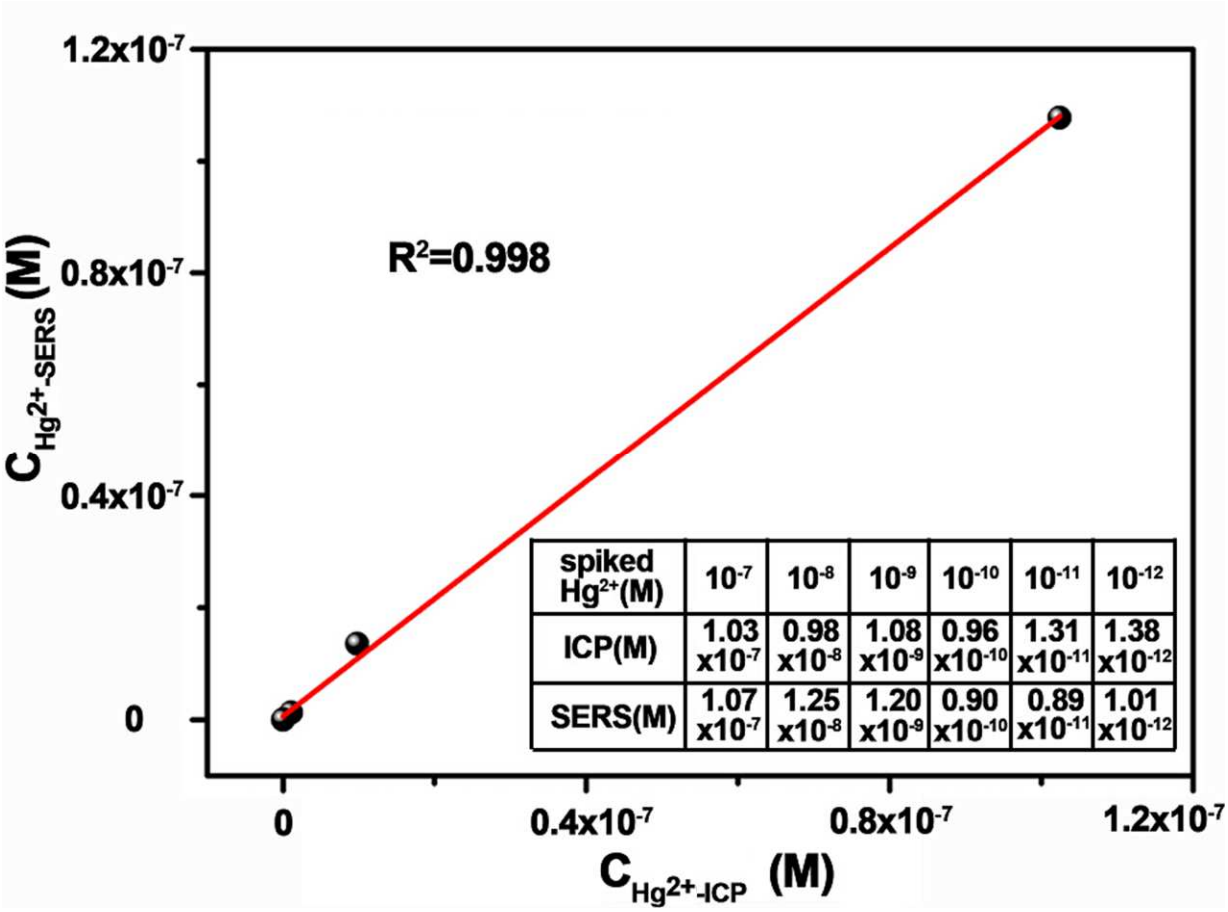

Figure S4. Hg^{2+} concentrations in river water samples determined by the classic ICP-AES method and our SERS sensor. According to the linear fitting, there is a good correlation between the SERS sensor and ICP-AES, with the correlation coefficient R^2 of 0.998, indicating the Hg^{2+} concentrations detected by the SERS sensor are in good agreement with those determined by the ICP-AES strategy. For clear comparison, the values of Hg^{2+} concentrations obtained from the standard addition analysis, determined by the ICP and SERS methods are listed in the inset table.

Table S1. Oligonucleotides sequences for DNA detection in the experiment.

Oligonucleotides	Sequences
Stem-loop DNA	5´-Cy5-TTCTTTCTTCCCCTTGTTTGTT-SH-3´
Interfering DNA	5´-TGAGTGGACGTCAACGAGCAA-3´

Table S2. Comparison of different SERS methods for the detection of Hg^{2+}.

SERS substrate[a]	Sensing mode	LOD[b]	RSD[c]	Ref.
AuNPs/grapheme heterojunction	Turn on	0.1 nM	~12%	5
ZnO/Ag nano-arrays	Turn off	2.25 nM	~17%	6
Nanoporous Au film	Turn off	1 pM	not mentioned	7
Au nanowire on Au film	Turn on	100 pM	not mentioned	8
AuNPs@SiNWAr	Turn on	1 pM	~9%	This work

[a]AuNPs@SiNWAr, gold nanoparticles (AuNPs) decorated silicon nanowire array (SiNWAr).[b]LOD, limit of detection. [c]RSD, relative standard derivation, is served as the acknowledged indicator of reproducibility to evaluate whether it's good or not. Typically, RSD value less than 15% in the SERS method can be considered as good reproducibility.[9,10]

In summary, compared to previously reported results, our SERS sensor is quantifiably demonstrated to have both high sensitivity (LOD: 1 pM) and good reproducibility (RSD: 9%).

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