Electronic Supplementary Material (ESI) for Analyst.

SUPPORTING INFORMATION

Ultrasensitive SERS detection of specific oligonucleotides based on Au@AgAg bimetallic nanorods

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Supporting figures and tables

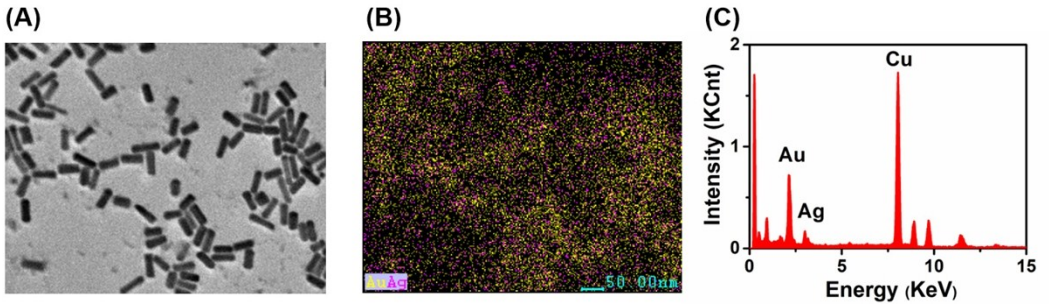

Fig. S1. (A) TEM image of Au@AgAgNR, (B) chemical mapping image, (C) EDS spectrum.

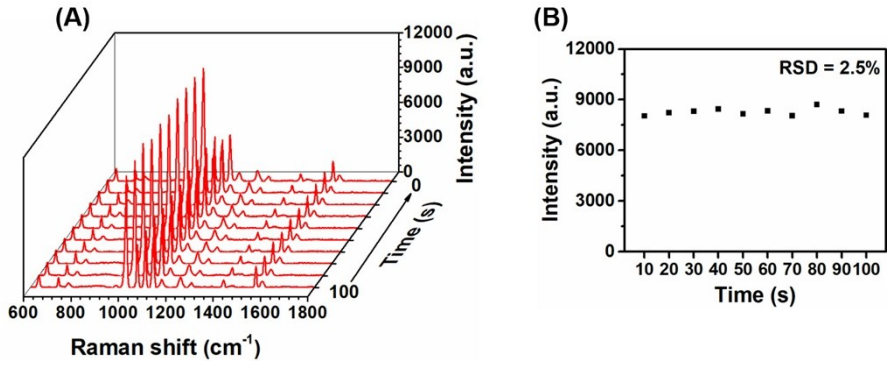

Fig. S2. (A) Time-dependent Raman results of 2-Mpy-encoded Au@AgAgNR nanotags. The concentration of the nanotags was 5 nM, 20 µL. (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A).

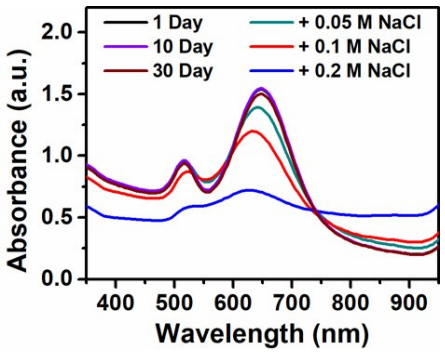

Fig. S3. The colloidal stability of Au@AgAgNR in solution monitored by UV-vis absorption, the colloidal of initial day showing a freshly made dispersion as well as those left for 10, and 30 days, and after different concentrations of NaCl were added.

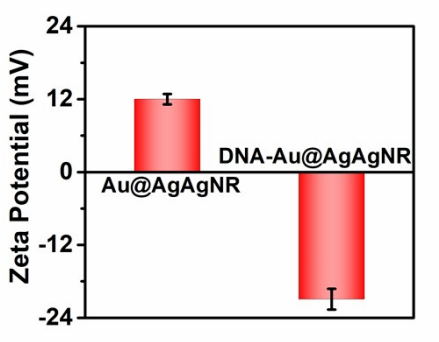

Fig. S4. Zeta potential measurement of original Au@AgAgNR (left) and DNA-modified Au@AgAgNR (right).

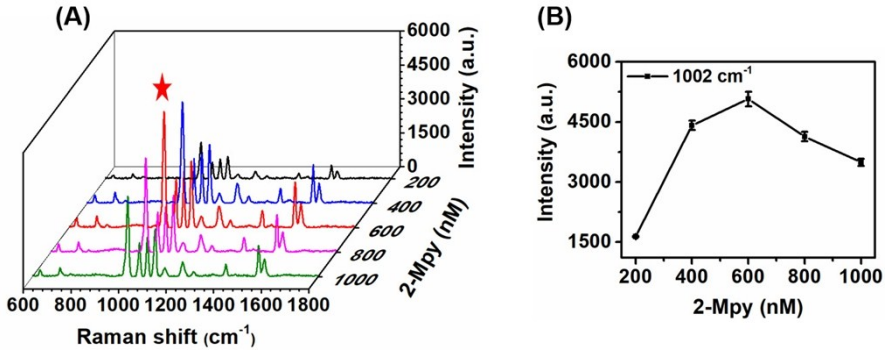

Fig. S5. (A) SERS spectra of AuNR with different concentrations of 2-Mpy. (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A).

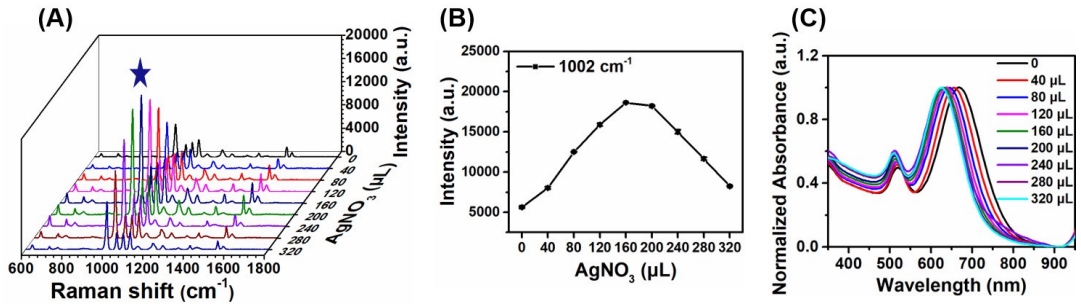

Fig. S6. (A) SERS spectra of 6×10^{-7} M 2-Mpy molecules in Au@AgNR with different volume of $AgNO_3$ (10 mM). (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A). (C) Normalized UV-vis absorption spectra of the Au@AgNR with different volumes of $AgNO_3$ (10 mM).

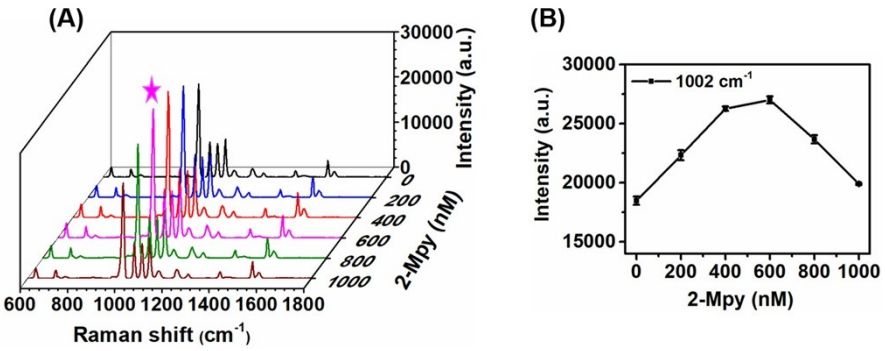

Fig. S7. (A) SERS spectra of Au@AgNR with different concentrations of 2-Mpy. (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A).

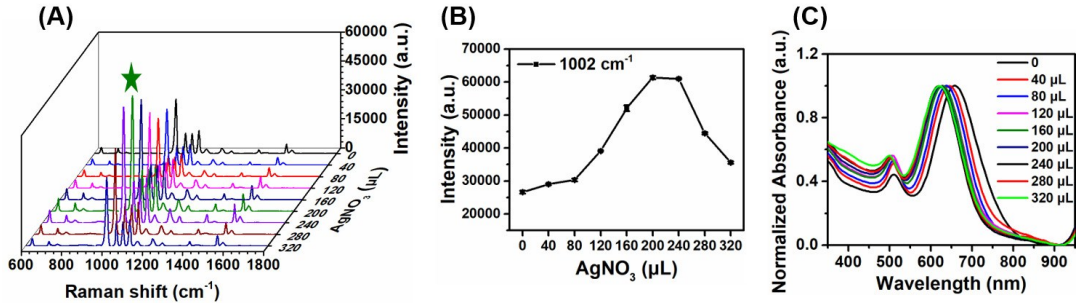

Fig. S8. (A) SERS spectra of 6×10^{-7} M 2-Mpy molecules in Au@AgAgNR with different volume of $AgNO_3$ (10 mM). (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A). (C) Normalized UV-vis absorption spectra of the Au@AgAgNR with different volumes of $AgNO_3$ (10 mM).

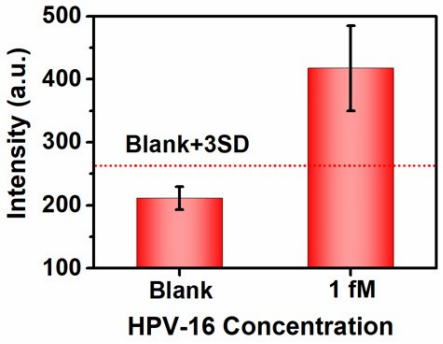

Fig. S9. Bar graphs showing the LOD of HPV-16 assay. The dashed lines indicate the threshold (Blank + 3SD).

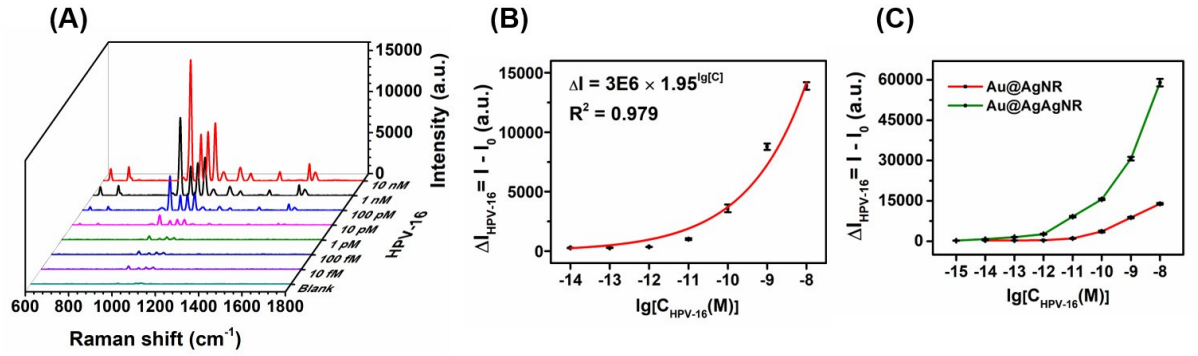

Fig. S10. (A) SERS spectra of 2-Mpy for quantitative evaluation of HPV-16 with different concentrations using Au@AgNR nanotags. (B) Plot of change in Raman intensity at 1002 cm^{-1} as a function of the logarithm of HPV-16 concentration is nonlinear from 10 fM to 10 nM using Au@AgNR nanotags. (C) Comparison of signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} for quantitative evaluation of HPV-16 with different concentrations using Au@AgNR and Au@AgAgNR nanotags, respectively.

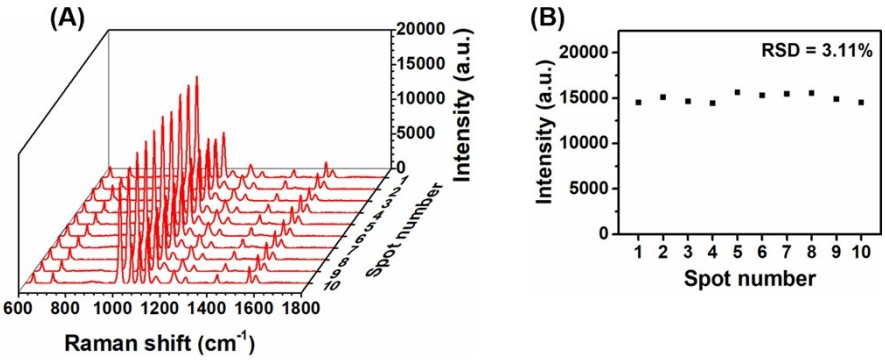

Fig. S11. (A) SERS spectra of 2-Mpy collected at 10 randomly selected spots on the sandwich-type complexes. (HPV-16: 100 pM). (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A).

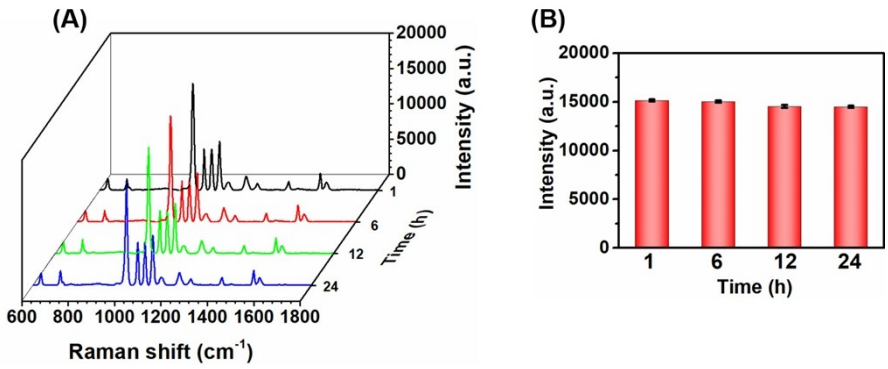

Fig. S12. (A) The SERS spectra of 2-Mpy within 24 h (HPV-16: 100 pM). (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A).

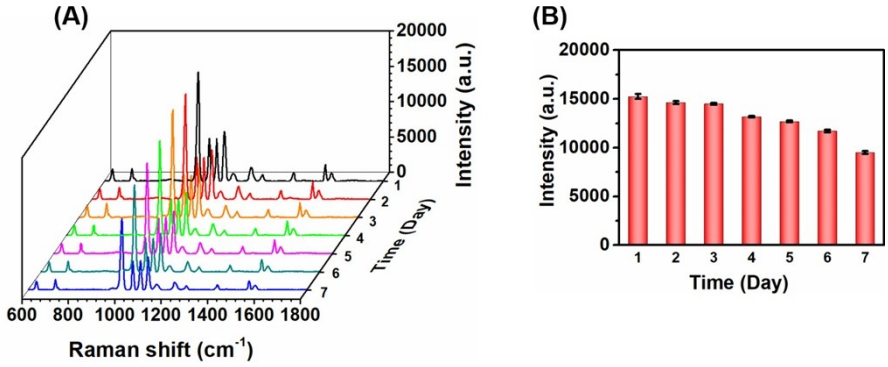

Fig. S13. (A) The SERS spectra of 2-Mpy over a 7-day period (HPV-16: 100 pM). (B) Signal intensities of 2-Mpy characteristic peak at 1002 cm^{-1} from the data in (A).

Table S1. Sequences of oligonucleotides used in this work.

Oligonucleotides	Sequences (5'-3')
HPV-16	TCTGAAGTAGATATGGCAGCACATAATGAC
DNA1	SH-$(CH_2)_6$- TTTTTTTTTTGTCATTATGTGCTGC
DNA2	CATATCTACTTCAGATTTTTTTTTT -$(CH_2)_6$-biotin
HPV-18	TGCCCAGGTACAGGAGACTGTGTAGAAGCA
HPV-52	TTTATATGTGCTTTCCTTTTTAACCTCAGCA
A mismatch	TCTGAAGAAGATATGGCAGCACATAATGAC
G mismatch	TCTGAAGGAGATATGGCAGCACATAATGAC
C mismatch	TCTGAAGCAGATATGGCAGCACATAATGAC

Table S2. Comparison of different nanomaterial-based methods for the detection of oligonucleotides

Detection method	Nanomaterial	Detection range	LOD	Reference
SERS	Au NPs	1 nM ~ 100 nM	1 nM	1
SERS	Au@Ag-tGO-Au@Ag	0 ~ 1 nM	10 pM	2
SERS	pA-nF-NTs-MMPs	10 pM ~ 100 nM	0.18 pM	3
SERS	Au-Ag nanomushrooms-MMPs	10 fM ~ 100 pM	10 fM	4
SERS	Au-RNNPs@Ag-HMSs	10 fM ~ 100 nM	10 fM	5
SERS	Au@PMPs	20 nM ~ 100 nM	10 fM	6
SERS	Au island@glass	1 fM ~ 10 nM	1 fM	7
SERS	AgNPs@Si	1 fM ~ 100 pM	1 fM	8
SERS	Fe_3O_4@Ag NPs	0 ~ 1 nM	0.3 fM	9
SERS	Au NPs-MB	1 fM ~ 100 nM	0.17 fM	10
SERS	DIP-MMPs	10 aM ~ 1 pM	10 ~ 100 aM	11
PCR-SERS	Ag colloids	1 pM ~ 100 pM	10 pM	12
Colorimetry	Ag NPs	20 nM ~ 2500 nM	1.03 nM	13
SERS	Au@AgAgNR-MBs	1 fM ~ 10 nM	1 fM	This work

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