Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Sharp-featured Au@Ag Core/shell Nanocuboids Synthesis and the Label-free Ultrasensitive SERS Detection of Protein Single-point Mutation

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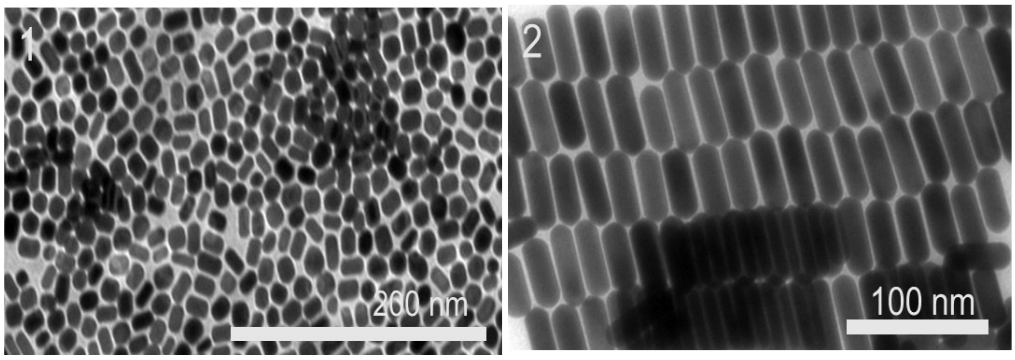

Figure S1. TEM images of the two sets of original gold NRs synthesized using sodium salicylate (on the right), and sodium oleate (left) as the additive.

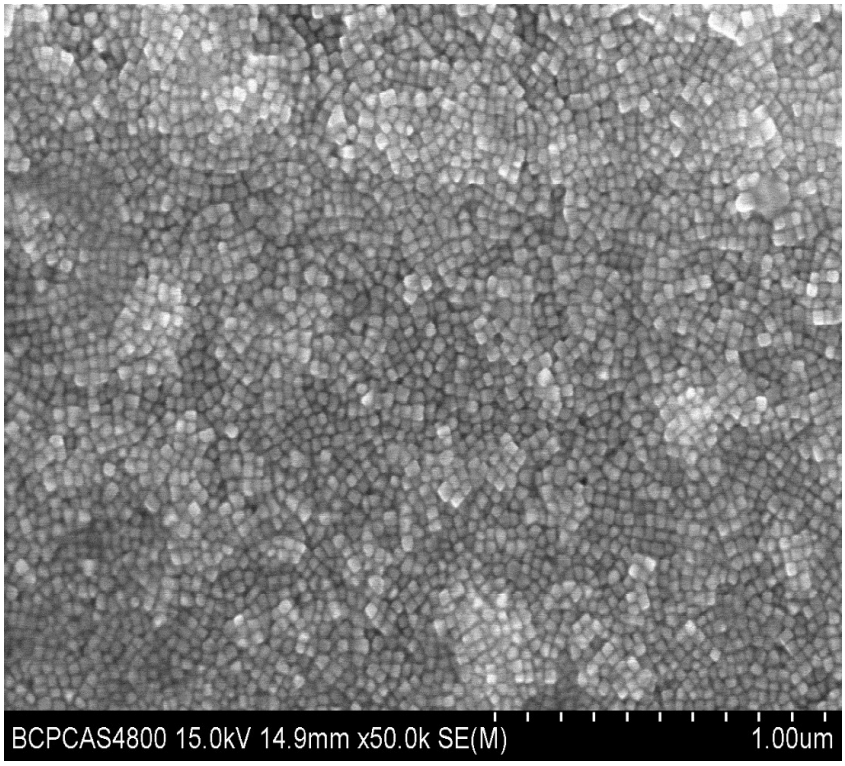

Figure S2. Large scale SEM image of the as prepared Au@Ag nanocuboids with Au-1 NRs.

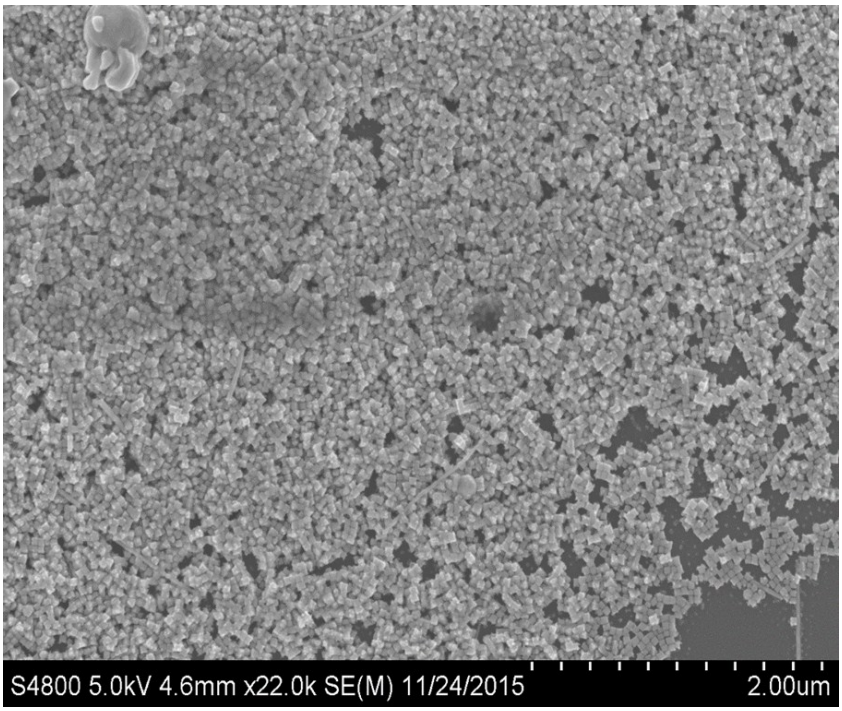

Figure S3. Large scale image of Au@Ag nanocuboids prepared with Au-2 NRs.

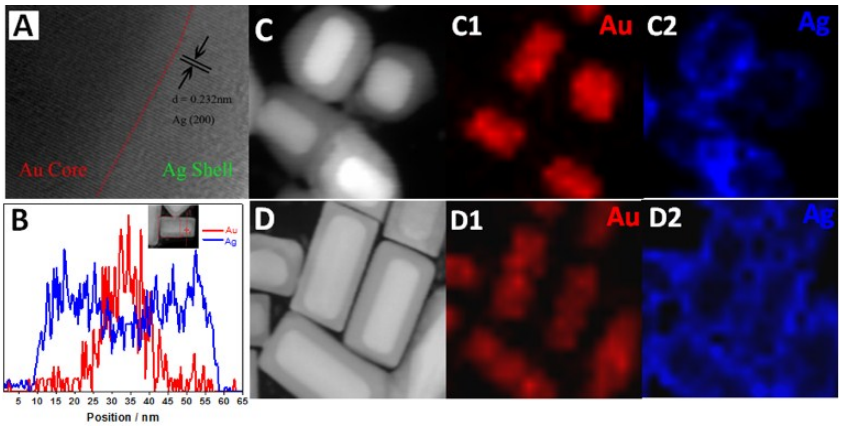

Figure S4. (A) HRTEM images of typical Au@Ag core/shell NCs; (B) Line scanning of the Au@Ag core/shell NCs; (C and D) EDS elemental mapping of Au@Ag core/shell NCs with AR = 1 and 2, respectively.

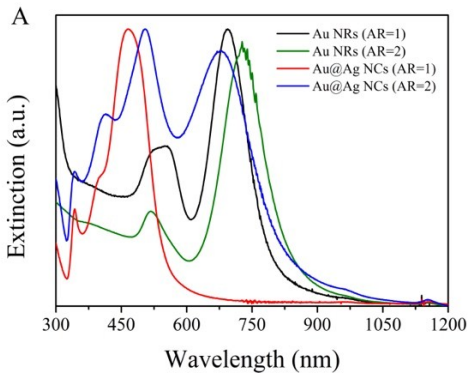

Figure S5. UV-Vis-NIR spectra of Au-1 NRs (black), Au-2 NRs (green) and Au@Ag-1 NCs (red), Au@Ag-2 NCs (blue) colloids.

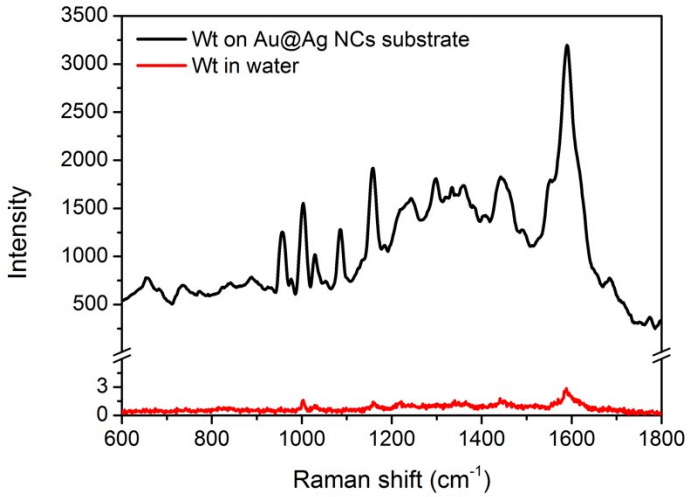

Figure S6. SERS spectra of Wt (10 pM) on Au@Ag NCs assembly (black) and Raman spectra of Wt (1 mM) in water (red).

SI-1 Calculation for enhancement factors:

Enhancement factor (EF) for Au@Ag-1 NCs substrate was estimated using the expression EF = (I_{SERS} / $I_{solution}$) × ($N_{solution}$ / N_{SERS}).[1] EF is calculated by direct comparison of the intensities provided by the SERS (I_{SERS}) and solution Raman ($I_{solution}$) experiments and the total number of molecules in the SERS (N_{SERS}) and solution Raman ($N_{solution}$) experiments. A concentrated Wt protein solution (1 mM in DI water) was measured by using the solution Raman experiment under the same conditions that the experiments carried out Au@Ag-1 NCs. The light spot diameter of the SERS laser was 2 μm. The size of the quartz cell used for solution Raman experiment was 1 × 1 × 3 cm. The I_{SERS} and $I_{solution}$ at 1590 cm^{-1} were 3195.5 and 2.84, respectively.

Reference for SI-1：

1. Mulvihill, M. J.; Ling, X. Y.; Henzie, J.; Yang, P. *J. Am. Chem. Soc.* **2010**, 132, 268.

Wt TDP-43:
H_2N-QGGFGNSRGGGAGLGNNQGSNMGGGMNFGAFSINPAMMAAAQAALQ-COOH
pA315T TDP-43: H_2N-
QGGFGNSRGGGAGLGNNQGSNMGGGMNFGT(p)FSINPAMMAAAQAALQ-COOH
A315E TDP-43:
H_2N-QGGFGNSRGGGAGLGNNQGSNMGGGMNFGEFSINPAMMAAAQAALQ-COOH

Scheme S1 The sequences for Wt, pA315T and A315E TDP-43. The red capital letters ‘‘A’’, ‘‘T’’, and ‘‘E’’ highlight the mutation site, and ‘‘p’’ in the bracket points out the phosphorylated residue Thr315 for pA315T TDP-43.

Table S1 Assignment of bands in SERS spectra of TDP-43 and IAPP8-37 protein

Wavenumber (cm^{-1})	Assignment	Ref.
823	Tyr	1-2
850-856	Tyr	1-2
899-902	Pro	3
957-960	C-C stretching	1-2, 4
1000-1004	Phe	1-2, 4
1030-1036	Phe	1-2, 4
1080-1089	Lys, Arg, Gln, Asn	2
1124	Val, Ile	2
1154-1160	C-N stretching	1-2, 4
1218-1220	$-CH_3$ bending	1-2, 5
1240-1246	Amide III (β-sheet)	1-2
1262-1265	Amide III (α-helix, random coil)	1-2
1325-1336	$-CH_2$ twist/wag	1-2, 5
1443-1455	$-CH_2$ bending	1, 4
1479-1485	His	1, 2
1522	Amide III	4
1588-1592	Phe	1-2

Reference for Table S1：

1. Chou, I. H.; Benford, M.; Beier, H. T.; Coté G. L. *Nano Lett.* **2008**, 8, 1729.
2. Choi, I.; Huh, Y. S.; Erickson, D. *Microfluid Nanofluid* **2012**, 12, 663.
3. Kurouski, D.; Deckert-Gaudig, T.; Deckert, V.; Lednev, I. K. *J. Am. Chem. Soc.* **2012**, 134, 13323.

4. Brulé, T.; Yockell-Lelievre, H.; Bouhelier, A.; Margueritat, J.; Markey, L.; Leray, A.; Dereux, A.; Finot, E. *J. Phys. Chem. C* **2014**, 118, 17975.

5. Podstawka-Proniewicz, E.; Piergies, N.; Skozuba, D.; Kafarski, P.; Kim, Y.; Proniewicz, L. M. *J. Phys. Chem. A* **2011**, 115, 11067.