Electronic Supplementary Material (ESI) for Analytical Methods.

Supplementary Information

Interface engineering with self-assembling Au@Ag@β-cyclodextrin bimetal nanoparticles to fabricate ring-like arrayed SERS substrate for sensitive recognition of phthalate esters based on host-guest interaction and the coffee ring effect

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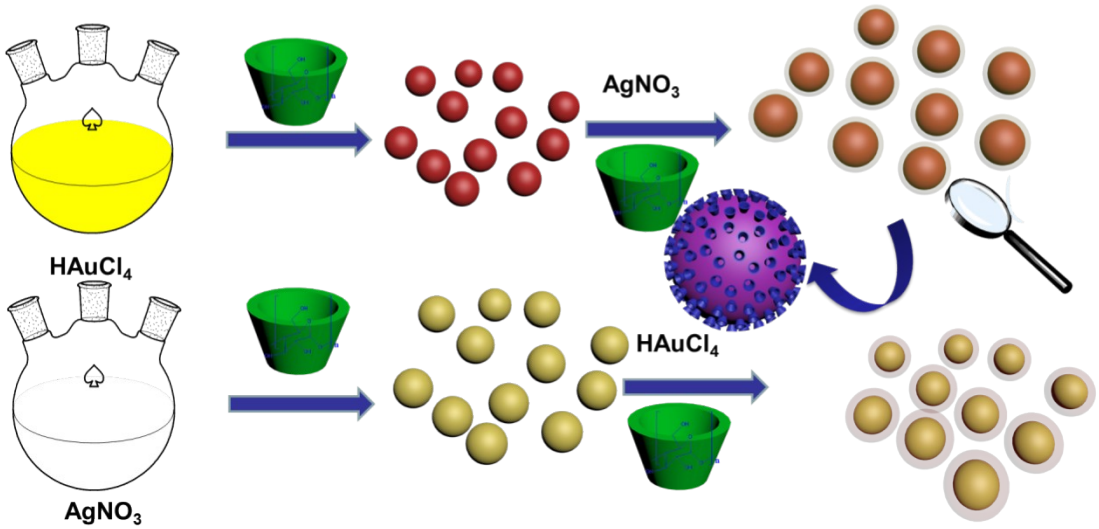

Scheme S1 Schematic illustration of the synthesis of Au@Ag@β-CD and Ag@Au@β-CD core-shell nanoparticles.

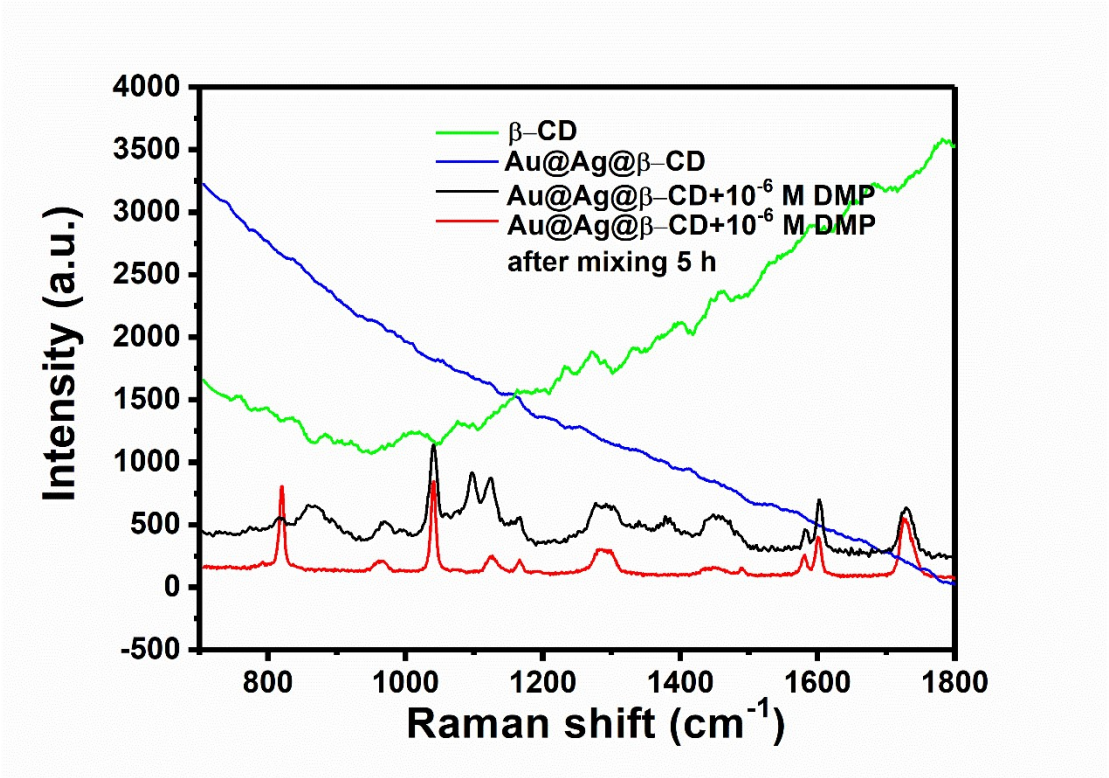

Figure S1. SERS spectra of β-CD, Au@Ag@β-CD, Au@Ag@β-CD-10^{-6} M DMP and Au@Ag@β-CD-10^{-6} M DMP after mixing 5 h.

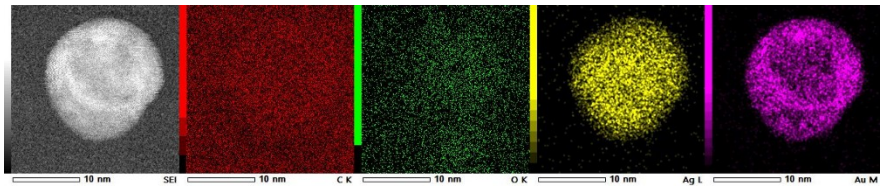

Figure S2. STEM-EDS elemental mapping images of Agcore@Aushell@β-CD

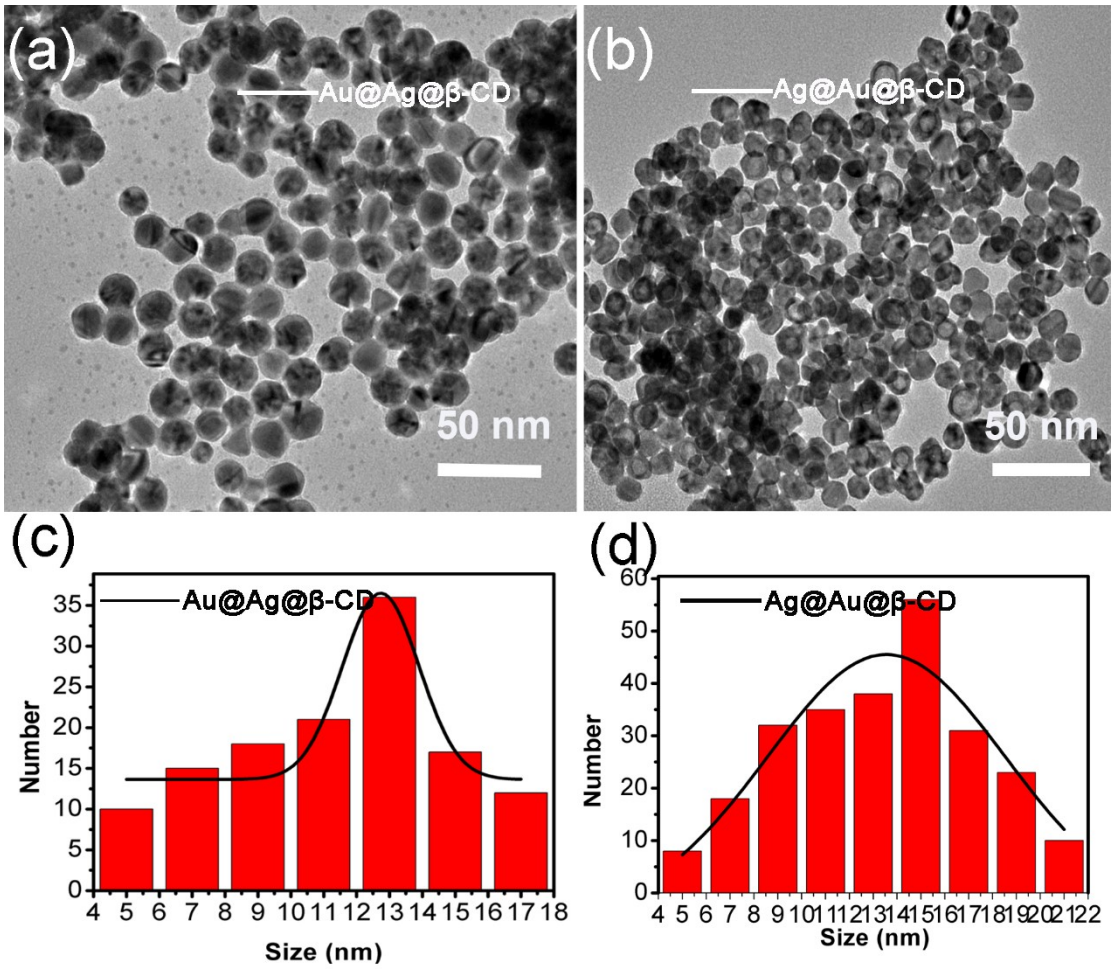

Figure S3. Low magnification TEM images of (a) Au@Ag@β-CD and (b) Ag@Au@β-CD core-shell nanoparticles; the corresponding particle size distribution curves of (c) Au@Ag@β-CD and (d) Ag@Au@β-CD core-shell nanoparticles.

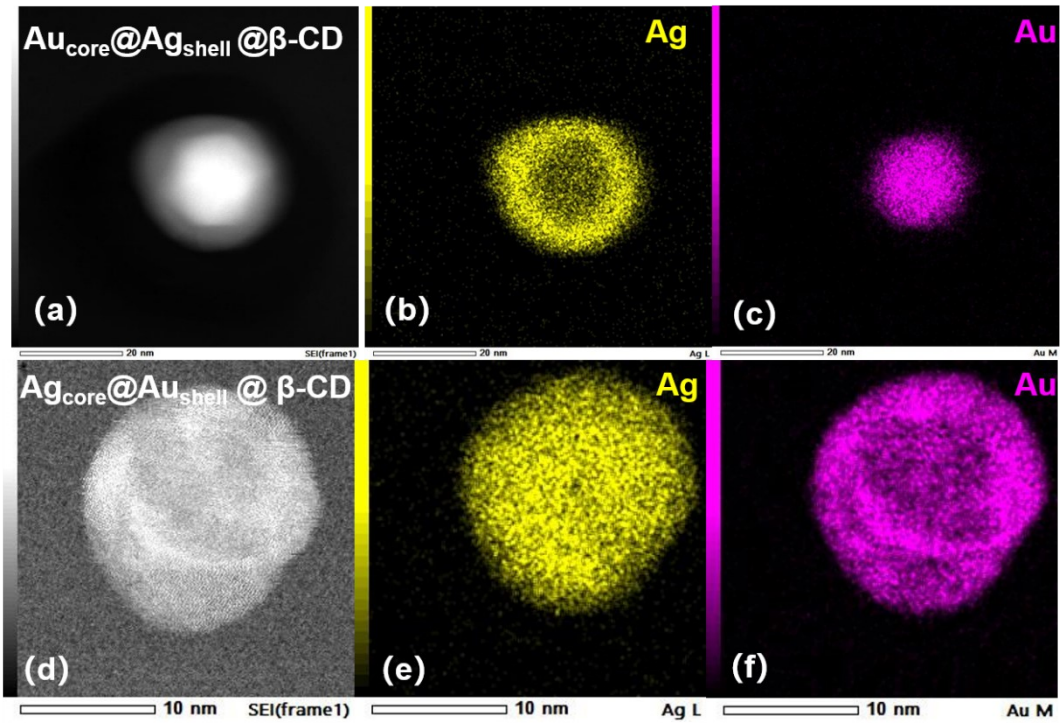

Figure S4. SEM-EDS elemental mapping images of (a-c) Au@Ag@β-CD and (d-f) Ag@Au@β-CD nanoparticles

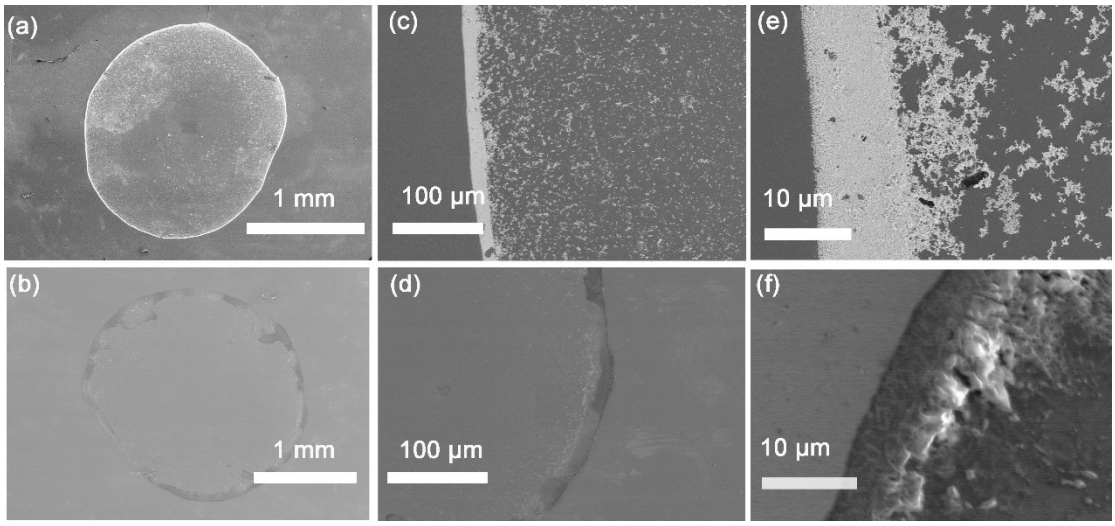

Figure S5. The gradually enlarged SEM images of the ring-like Ag@Au@β-CD SERS substrate (a, c, e) and the ring-like Au@Ag@β-CD SERS substrate (b, d, f).

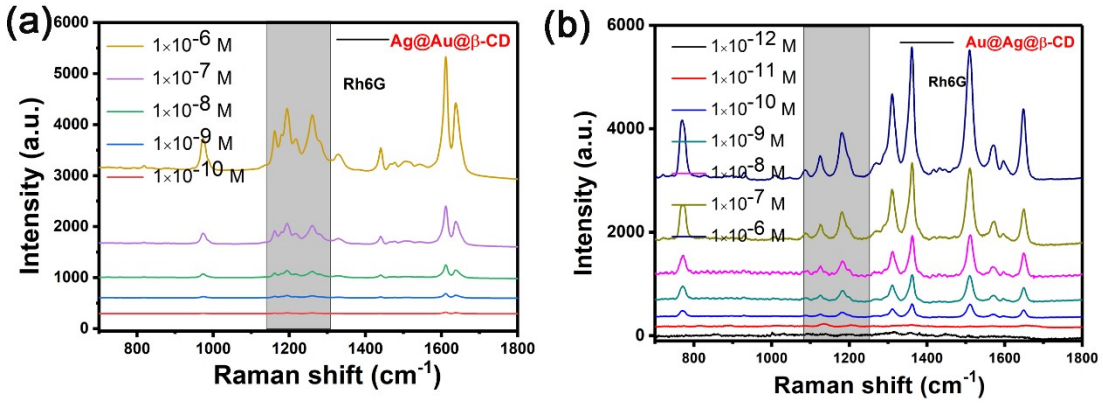

Figure S6. Concentration-dependent SERS spectra of (a) the ring-like Ag@Au@β-CD and (b) the ring-like Au@Ag@β-CD SERS substrates with various concentrations of Rh6G(1×10^{-6} M，1×10^{-7} M, 1×10^{-8} M, 1×10^{-9} M, 1×10^{-10} M, 1×10^{-11} M，1×10^{-12} M).

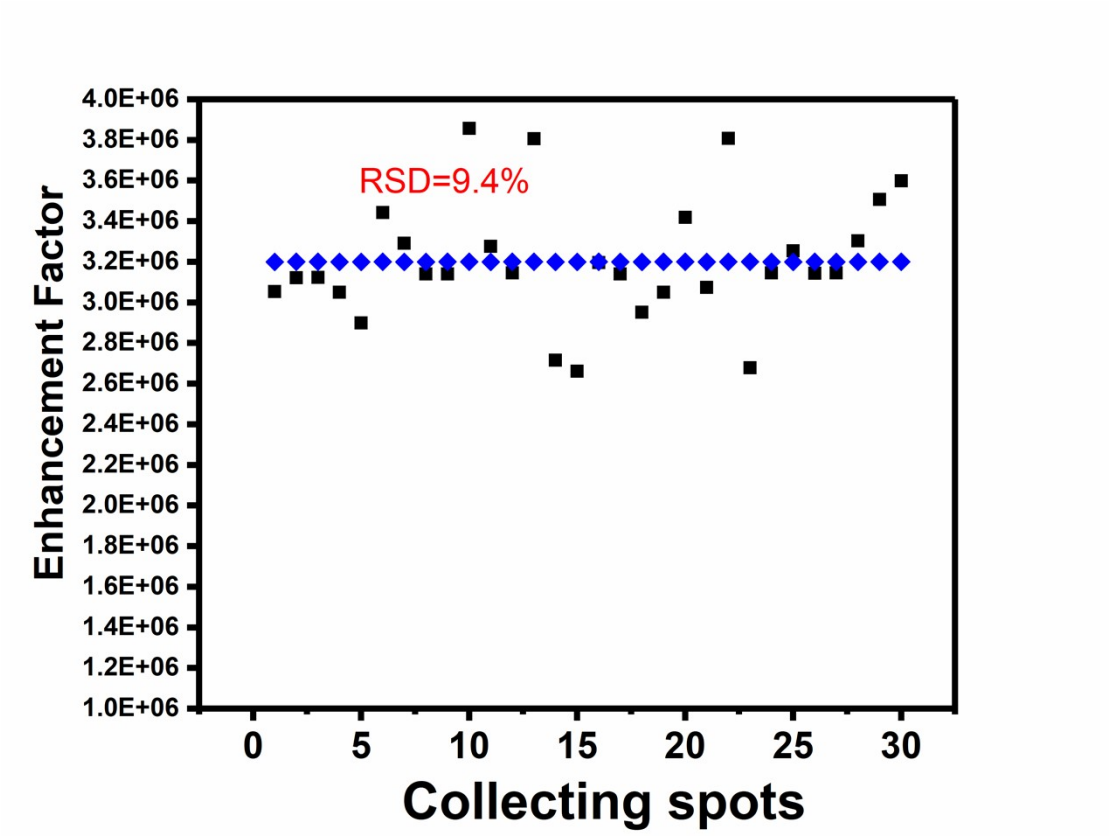

Figure S7. The standard deviation of EF of the ring-like Au@Ag@β-CD SERS substrate

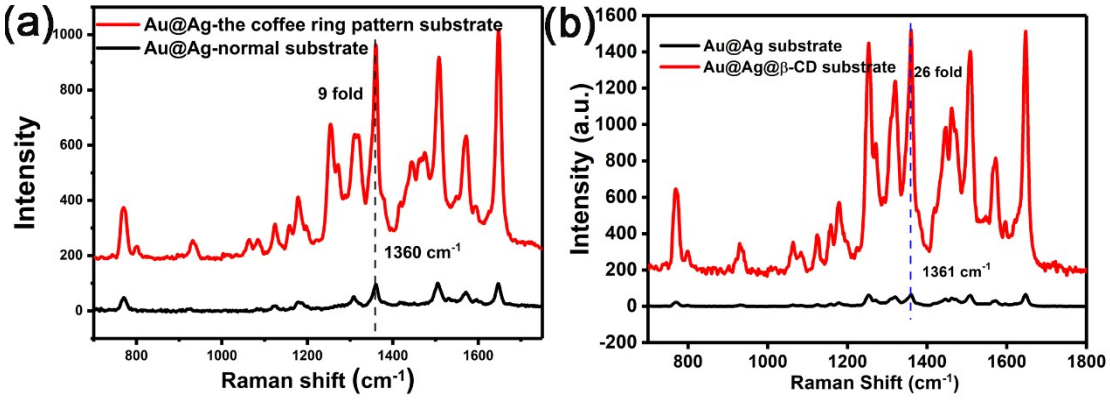

Figure S8. (a) Comparison of SERS intensity between ring-forming and non-ring-forming normol substrates with concentration of 1×10^{-8} M Rh6G. (b) Comparison of SERS intensity of the coffee ring substrates formed by modified β-CD and unmodified β-CD Au@Ag nanoparticles with concentration of 1×10^{-8} M Rh6G.

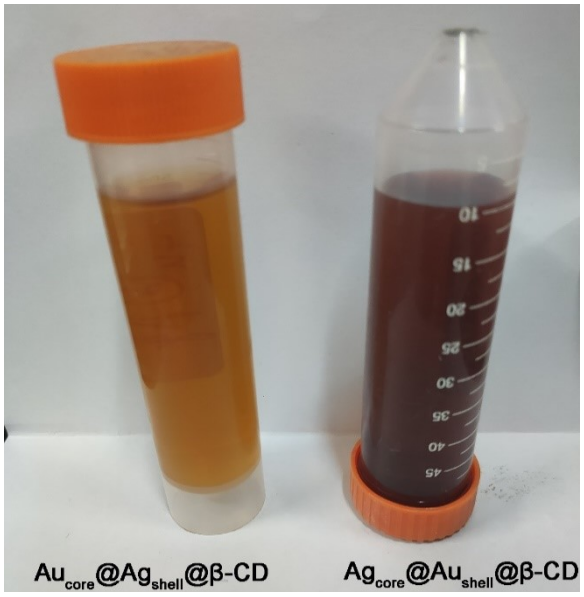

Figure S9. the photograph of Ag@Au@β-CD and Au@Ag@β-CD suspensions solution

Table S1. Detection of DOP in tap water and river water (n=5)

Sample	**Added (nM)**	**Found (nM)**	**Recovery (%)**	**RSD (%) (n=5)**
tap water	5	4.76	95.2	5.32
	20	21.32	106.6	5.62
	50	48.56	94.1	4.79
river water	5	4.68	93.6	5.83
	20	18.95	94.5	4.14
	50	46.32	92.3	3.86

Table S2. Comparison of our proposed SERS method and previous reported SERS methods for the detection of PAEs

SERS-active substance	Test sample	PAE	Detection limit	Recovery (%)	RSD (%)	Refs
SiO_2@Au/Ag	Standard sample	DOP DBP	0.24 nM 0.22 nM	none	none	1
Au@Ag NCs	Standard sample	BBP DEHP	1.3 ng	none	none	2
Au NPs	Standard sample	DBP	1.3 μg			3
AuNPs@β-CD	Liquors and rice wine	BBP	14.9 nM	90~108	1.9~11.7	4
Au NPs	Standard sample	DOP	10 nM			5
Au@Ag@β-CD NPs	Tap and river water	DOP	0.2 nM	92~106.6	3.86~5.62	Our work

References:

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2.Hu X, Wang X, Ge Z, et al. Bimetallic plasmonic Au@ Ag nanocuboids for rapid and sensitive detection of Phthalate plasticizers with label-free Surface-enhanced Raman Spectroscopy[J]. Analyst, 2019.

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