Electronic Supplementary Material (ESI) for Analytical Methods.

Supporting Information

$Ag@SiO_2$ nanocubes-loaded miniaturized filter paper as Hybrid Flexible plasmonic SERS Substrate for trace Melamine Detection

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Synthetic Procedure for Ag@SiO_2NCs

First, the AgNCs were prepared by polyol method.[1, 2] Briefly, into a 100 mL round bottom flask, 20 mL ethylene glycol was added and heated in an oil bath pre-set at 150°C for 40 minutes under magnetic stirring. NaSH (240 µL, 3 mM in EG) was then quickly injected into the heated solution. Two minutes later, HCl (2 mL, 3 mM in EG was added into the heated reaction solution, followed by the addition of poly (vinyl pyrrolidone) (PVP, 5 mL, 20 mg/mL in EG). After another 2 min, silver trifluoroacetate (1.6 mL, 282 mM in EG) was added into the mixture. During the entire process, the flask was capped with a glass stopper except during the addition of reagents. After 40 minutes when the color of the reaction media turned into green–ocher, the reaction was quenched by placing it in an ice-water bath. Finally, after rinsing with acetone, the solution was centrifuged at 12000 rpm for 30 minutes. To remove the excess PVP and remaining precursor the precipitate was washed with deionized water four times and the product was re-dispersed in isopropanol and stored at 20°C for the next part of the experiment. For coating the AgNCs, a modified Stober method [1, 3, 4] was used Briefly, APS (20 µL, 1 mM-in 2-propanol) was added into 2 mL of Ag NCs solution and stirred for 30 min at 600 rpm at room temperature. Next, the mixture was dissolved in 6 mL of 2-propanol and stirred for 2 min, 2 mL of deionized water and 100 mL ammonia aqueous solution (35 % V/V) were added to the mixture. Next, TEOS (200 µL, 1 mM-in 2-propanol) was added dropwise with continuous stirring, and the reaction was allowed to continue for 6 hr. The product was collected by centrifugation and washing with ethanol once, and deionized water three times before being re-dispersed in deionized water.

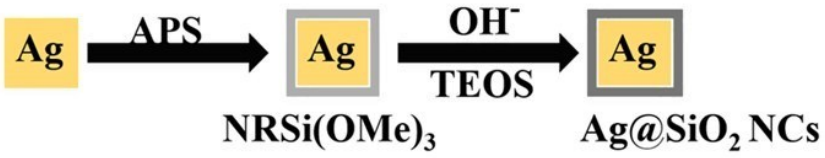

Figure S-1 Schematic illustration of Ag@SiO_2 nanocubes preparation

Table S-1: Raman peak assignment for R6G

Raman shift	**Peak assignment**
612 cm^{-1}	C–C–C ring in-plane vibration mode
772 cm^{-1}	C–H out of plane bending mode
1126 and 1181 cm^{-1}	C–H inplane bending
1362, 1507, 1642 cm^{-1}	C–C stretching of the aromatic ring
1311 and 1571 cm^{-1}	N–H inplane bending modes

Table S-2: Raman peak assignment for melamine

Raman shift	**Peak assignment**
378 cm^{-1}	N-C-N bending with NH_2 twisting
578 cm^{-1}	N-C-N bending with NH_2 wagging
684 cm^{-1}	in-plane deformation of the triazine ring (ring breathing mod II)
983 cm^{-1}	ring breathing mod I

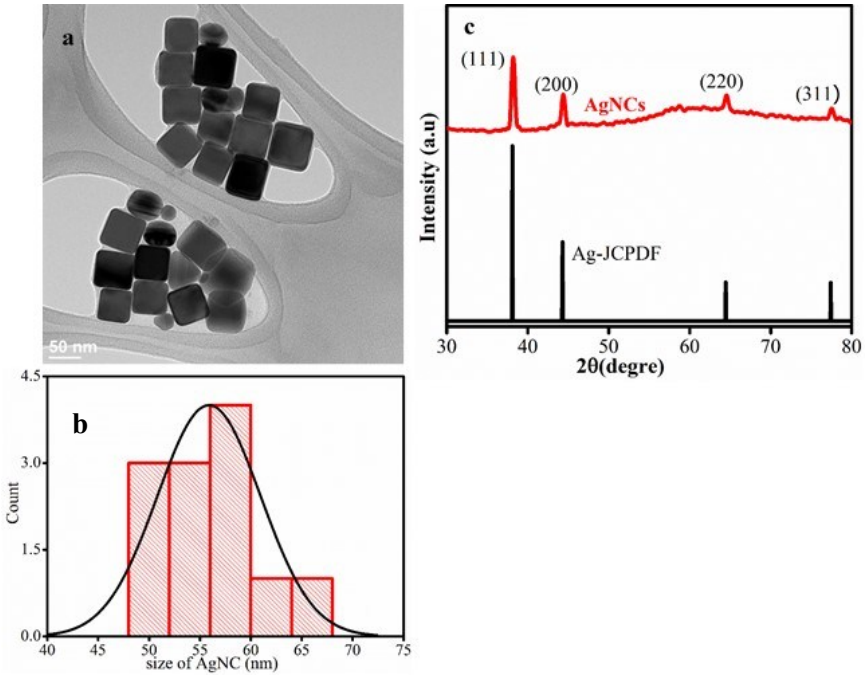

Figure S-2 (a) TEM image of Ag nanocubes; (b) particle size distribution of AgNCs; (c) XRD pattern of silver nanocubes

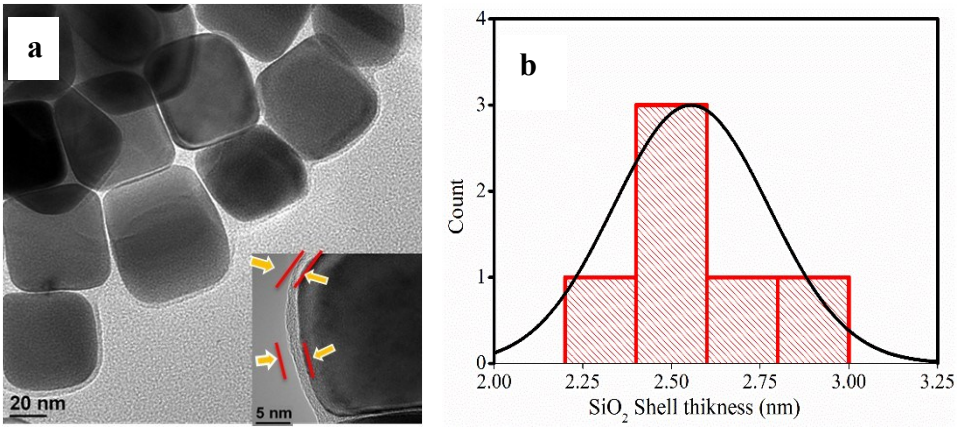

Figure S-3 (a) $Ag@SiO_2$ NCs; (b) distribution of the thickness of silica shell

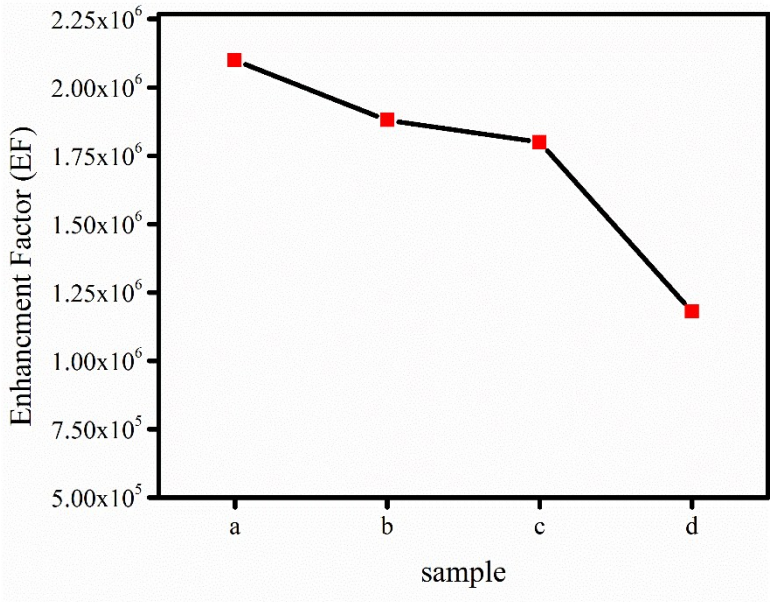

Figure S-4 Effect of the TEOS concentration on SERS activity (sample a=1 mM; sample b=4 mM; sample c= 8 mM; sample d=16 mM)

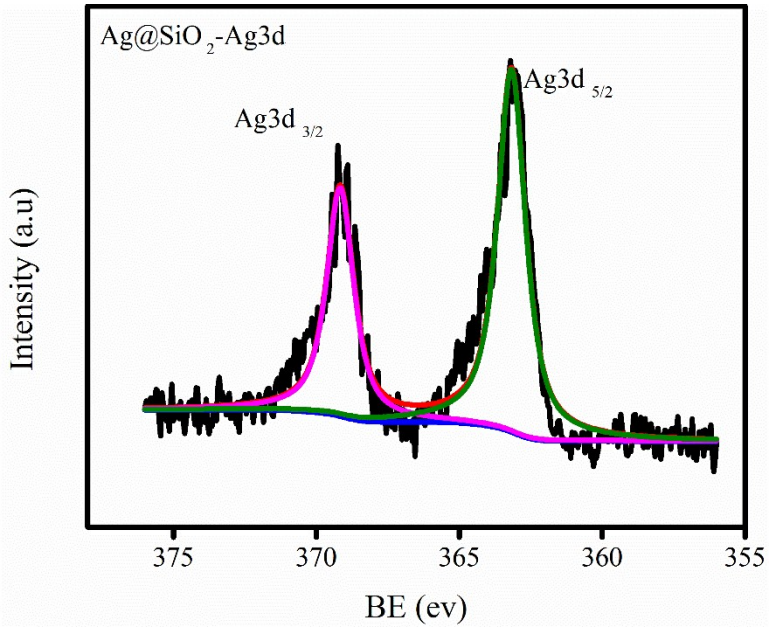

Figure S-5 High-resolution XPS spectrum of Ag3d

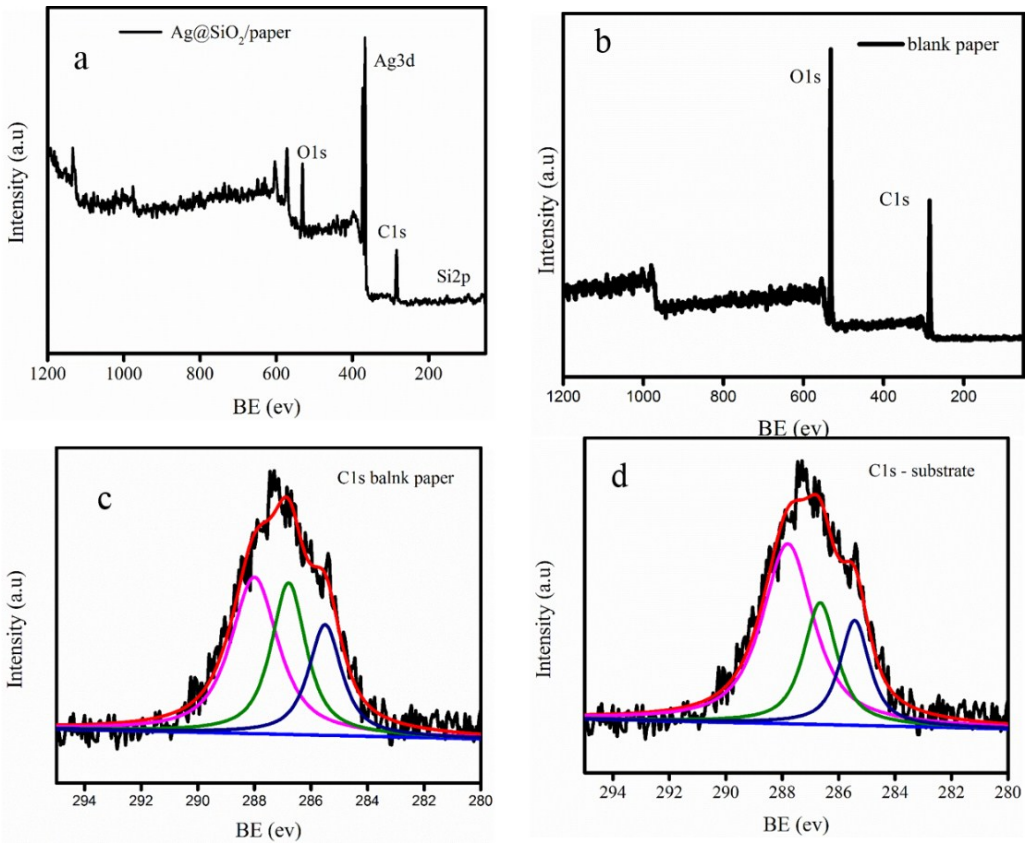

Figure S-6 (a) Wide scan XPS spectrum of the as-prepared substrate; (b) wide scan XPS spectrum of the blank filter paper; (c) C1s XPS spectrum of blank paper; (d) C1s XPS spectrum of the as-prepared substrate

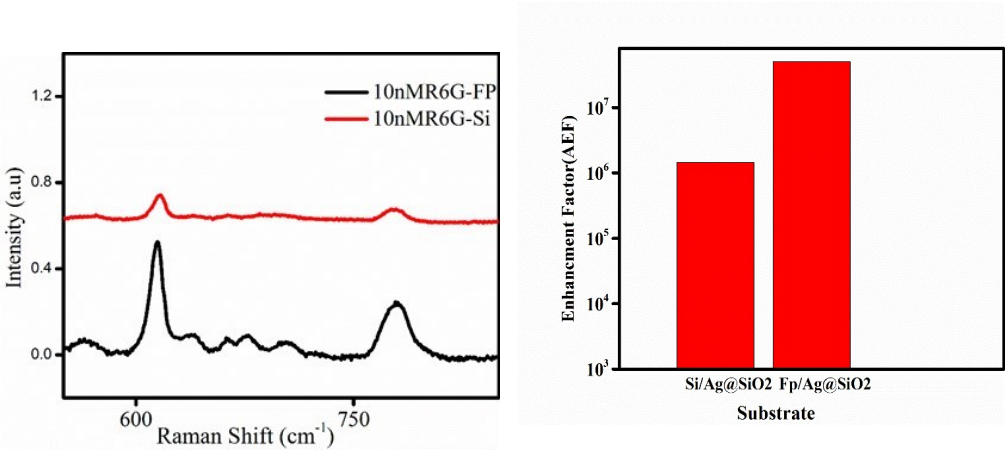

Figure S-7 (a) SERS spectra of 10 nM R6G on paper and Si-wafer substrate; **(**b) EF of paper and silica wafer substrates

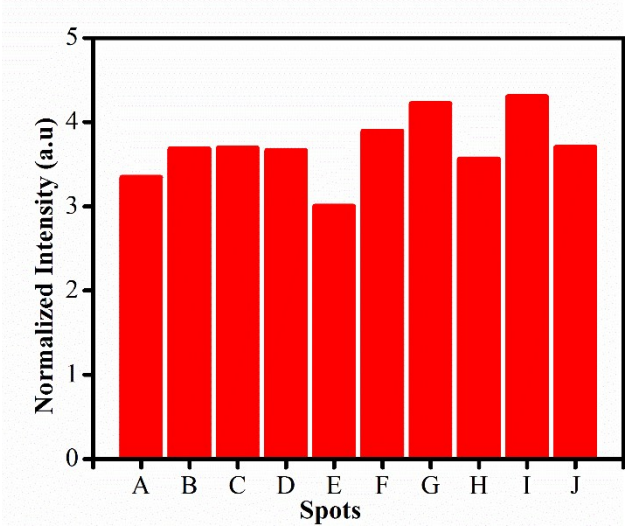

Figure S-8 Variability between spots within the same substrate (probe 10^{-6} M R6G, the intensity was normalized by Si wafer @ 520 cm^{-1}

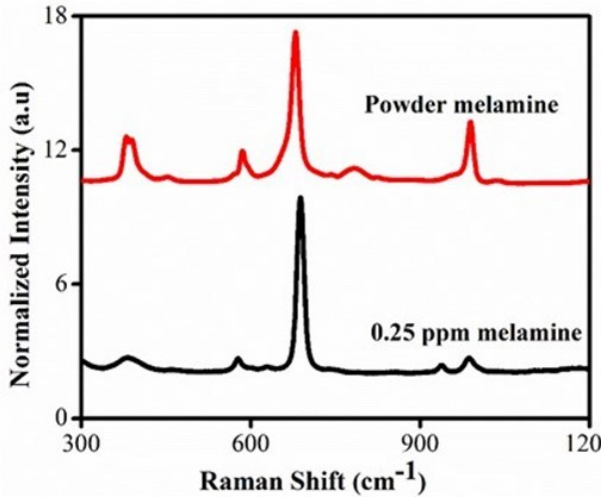

Figure S-9 Raman spectrum of powder melamine and SERS spectrum of 0.25 mg/L melamine

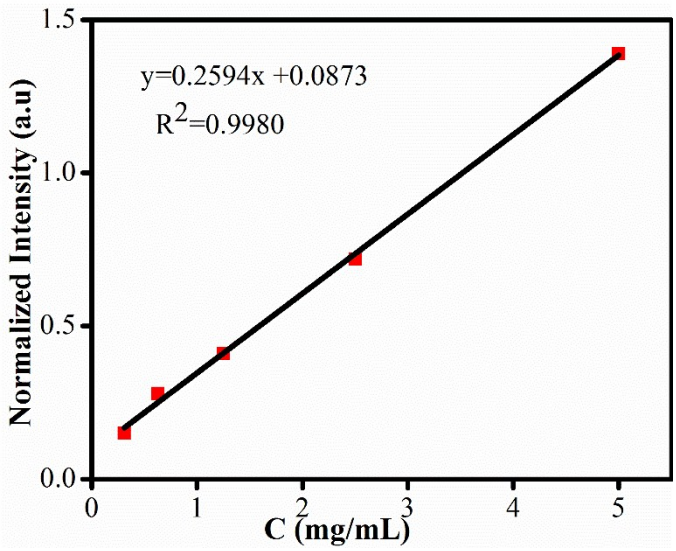

Figure S-10 SERS spectra of spiked milk (Figure 4 in manuscript) and the corresponding calibration curve

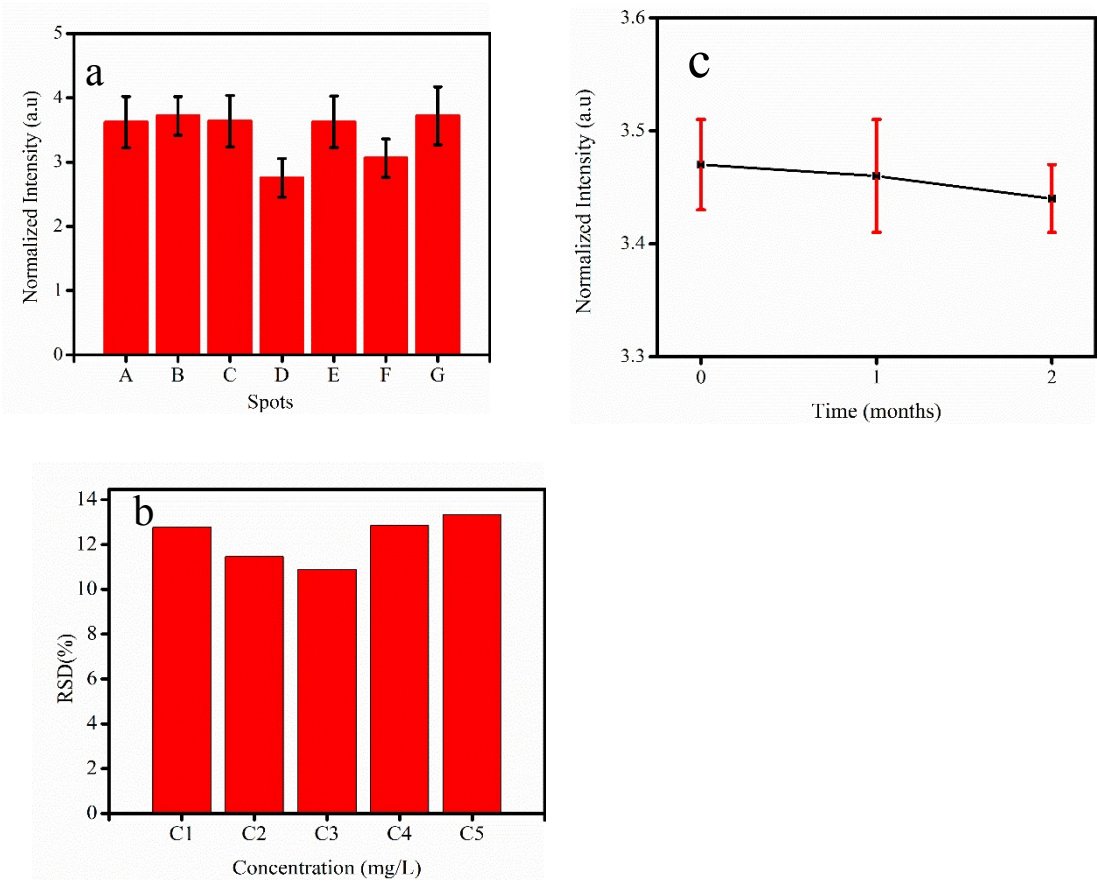

Figure S-11 (a) Variability tests of melamine at different spots on the same substrate (0.5 mg/L); (b) spot to spot variability of all the concentration levels of melamine standards (C1=0.063 mg/L, C2=0.125 mg/L C3=0.25 mg/L, C4=0.5 mg/L, C5=1 mg/L); (c) stability of the substrate tested at 0.5 mg/L

References

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