Glucose detection of 4-mercaptophenylboronic acidgold-silver core-shell assembled silica nanostructure by Surface enhanced Raman scattering.

Xuan-Hung Pham ^{1,} Bomi Seong ¹, Eunil Hahm ¹, Kim-Hung Huynh ¹, Yoon-Hee Kim ¹, Jaehi Kim ¹, Sang Hun Lee ², and Bong Hyun Jun ^{2,*}

- 1 Department of Bioscience and Biotechnology, Konkuk University, Seoul 05029, Republic of Korea
- 2 Department of Chemical and Biological Engineering, Hanbat National University, Daejeon 34158, Republic of Korea.
- * Correspondence: bjun@konkuk.ac.kr (B-H. J); Tel.: +82-2-450-0521 (B.H.J.)



Figure S1. (a) TEM images and (b) UV-Vis spectra of (i) SiO₂@Au (1 mg/mL) and (ii) SiO₂@Au@Ag nanostructures (20 μ g/mL) synthesized at 2 mg SiO₂@NH₂ and 300 mM Ag+ concentration.



Figure S2. (a) SERS spectra of SiO₂@Au@Ag@4-MPBA in PBST containing difference concentration of glucose (0-10 mM). (b) SERS spectra of SiO₂@Au@Au in ethanol in the presence of 50 μ M 4-mercaptophenylboronic acid, 50 μ M 4-mercaptophenylboronic acid + 1000 μ g/mL H₂O₂, 1 mM 4-mercaptophenol, 1 mM thiophenol.

Assignment	4-MPBA	4-MPheOH	4-MPBA
	in EtOH	in EtOH	in PBST
$8a(a_1), v_{CC}$		1597	
	1583	1583	1583
			1578
19a(a ₁), v _{CC}	1484	1484	1484
ν_{BO}	1346		
$3(b_2), \beta_{CH} + \beta_{BOH}$	1286		
$9a(a_1), \beta_{CH} + \beta_{BOH}$	1192		1192
		1170	
$1(a_1), \beta_{CCC} + \nu_{CS}$	1077		1077
18a(a ₁), β _{CH}			1025
12(a_1), β_{CCC}			999
10a(a ₂), γ_{CH}	820	824	824
11(b ₁), γ _{СН}	744	744	752
	728		
$6a(a_1), \beta_{CCC} + v_{CS}$	690		693
V _{CS}	632	625	638
$6b(b_1)$, β _{CCC}			612
16b(b ₁), β_{CCC}	473	473	473
$7a(a_1), \beta_{CCC} + \nu_{CS}$	417	417	417
		390	

Table S1. Raman frequencies and assignments of 4-MPBA and 4-MPheOH in EtOH and PBST

v: stretching; β : in-plane bending; γ : out-plane bending.



Figure S3. Normalized Raman intensity ratio of 20 μ g SiO₂@Au@Ag@4-MPBA in PBST containing various concentration of H₂O₂ in the range of 10⁻⁶ – 10³ μ g/mL at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077; (f) 1170/1583; (g) 1597/417; (h) 1597/1077 and (f) 1597/1583.



Figure S4. Normalized Raman intensity ratio of 20 μ g SiO₂@Au@Ag@4-MPBA in PBST containing 5 mM glucose and difference concentration of glucose oxidase in the range of $10^{-2} - 10^3 \mu$ g/mL at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077, (f) 1170/1583, (g) 1597/417, (h) 1597/1077 and (i) 1597/1583.



Figure S5. Normalized Raman intensity ratio of 20 μ g SiO₂@Au@Ag@4-MPBA in PBST containing 5 mM glucose and 100 μ g/mL glucose oxidase at different incubation time at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077, (f) 1170/1583, (g) 1597/417, (h) 1597/1077 and (i) 1597/1583.



Figure S6. Normalized Raman intensity ratio of SiO₂@Au@Ag@4-MPBA using different amount of SiO₂@Au@Ag (10 - 50 μ g) in PBST containing 5 mM glucose, 100 μ g/mL glucose oxidase for 1 hr at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077, (f) 1170/1583, (g) 1597/417, (h) 1597/1077 and (i) 1597/1583.



Figure S7. Normalized Raman intensity ratio of 20 μ g SiO₂@Au@Ag@4-MPBA in PBST containing 5 mM glucose, 100 μ g/mL glucose oxidase for 1 h and measure at different concentration of SiO₂@Au@Ag at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077, (f) 1170/1583, (g) 1597/417, (h) 1597/1077 and (i) 1597/1583.



Figure S8. Glucose detection by SiO₂@Au@Au@4-MPBA at optimized condition of 20 μ g SiO₂@Au@Ag, 100 μ g/mL glucose oxidase concentration for 1h and Raman measurement at 67 μ g/mL SiO₂@Au@Ag in PBST at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077, (f) 1170/1583, (g) 1597/417, (h) 1597/1077 and (i) 1597/1583.



Figure S9. Effect of interferences on SERS signal of SiO₂@Au@Ag@4-MPBA in 5 mM glucose by SiO₂@Au@Au@4-MPBA at optimized condition of 20 μ g SiO₂@Au@Ag, 100 μ g/mL glucose oxidase concentration for 1h and Raman measurement at 67 μ g/mL SiO₂@Au@Ag in PBST at (a) 390/417; (b) 390/1077; (c) 390/1583; (d) 1170/417; (e) 1170/1077, (f) 1170/1583, (g) 1597/417, (h) 1597/1077 and (i) 1597/1583.



Figure S10. Long-term storage of 200 μ g/mL SiO₂@Au@Ag@4-MPBA at 4°C in ethanol solution.