Electronic Supplementary Information

Au@SiO₂ Core-Shell Nanoparticles for Laser Desorption/Ionization Time of

Flight Mass Spectrometry

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1. SEM and TEM images of NPs

- 2. UV-vis absorption spectra of Au@SiO₂ CSNPs after the addition of aqueous solutions of HCl, NaOH, or NaCl
- 3. Graphs reflecting the optimization of LDI-TOF-MS analysis conditions based on Au@SiO₂ CSNPs
- 4. LDI-TOF-MS spectra based on Au@utSiO2 CSNPs

1. SEM and TEM images of NPs



Fig. S1 SEM images of 18 nm AuNPs at different magnifications (a and b), and SEM (c) and TEM (d) images of 50 nm AuNPs. The scale bars are 200 nm.



Fig. S2 SEM and TEM images of $Au@SiO_2$ CSNPs with different core sizes and shell thicknesses. a) SEM image, 18 nm core, 10 nm silica shell (scale bar: 100 nm); b) SEM image, 18 nm core, 20 nm silica shell (scale bar: 100 nm); c) TEM image, 50 nm core, 2~4 nm silica shell; d) SEM image, 50 nm core, 20 nm silica shell.

2. UV-vis absorption spectra of Au@SiO₂ CSNPs after the addition of aqueous



solutions of HCl, NaOH, or NaCl

Fig. S3 UV-vis spectra of Au@SiO₂ CSNPs with 18 nm Au core and different silica thicknesseses after the addition of HCl aqueous solutions with different concentrations. a) AuNPs, 0 nm silica shell; b) Au@utSiO₂ CSNPs, 2~4 nm silica shell; c) Au@SiO₂ CSNPs, 10 nm silica shell; d) Au@SiO₂ CSNPs, 20 nm silica shell. The initial concentration of NPs equals to 1.4 nM. The numbers in the legends represent the final concentration of HCl (mM) and they are arranged according to the descending of peak value (as shown by the arrows). The last number, which is the same as the penultimate one (with a dot on the right side), represents the system of the penultimate one after standing for another 30 minutes. The red dot lines represent the maximum concentration while the NPs are not congregated.



Fig. S4 UV-vis spectra of Au@SiO₂ CSNPs with 18 nm Au core and different silica thicknesses after the addition of NaOH aqueous solutions with different concentrations. a) AuNPs, 0 nm silica shell; b) Au@utSiO₂ CSNPs, 2~4 nm silica shell; c) Au@SiO₂ CSNPs, 10 nm silica shell; d) Au@SiO₂ CSNPs, 20 nm silica shell. The initial concentration of NPs equals to 1.4 nM. The numbers in the legends represent the final concentration of NaOH (mM) and they are arranged according to the descending of peak value (as shown by the arrows). The last number, which is the same as the penultimate one (with a dot on the right side), represents the system of the penultimate one after standing for another 30 minutes. The red dot lines represent the maximum concentration while the NPs are not congregated.



Fig. S5 UV-vis spectra of Au@SiO₂ CSNPs with 18 nm Au core and different silica thicknesses after the addition of NaCl aqueous solutions with different concentrations. a) AuNPs, 0 nm silica shell; b) Au@utSiO₂ CSNPs, $2\sim4$ nm silica shell; c) Au@SiO₂ CSNPs, 10 nm silica shell; d) Au@SiO₂ CSNPs, 20 nm silica shell. The initial concentration of NPs equals to 1.4 nM. The numbers in the legends represent the final concentration of NaCl (mM) and they are arranged according to the descending of peak value (as shown by the arrows). The last number, which is the same as the penultimate one (with a dot on the right side), represents the system of the penultimate one after standing for another 30 minutes. The red dot lines represent the maximum concentration while the NPs are not congregated.

3. Graphs reflecting the optimization of LDI-TOF-MS analysis conditions based on



Au@SiO₂ CSNPs

Fig. S6 MALDI-TOF-MS of dPEG6 based on CHCA in the absence (a and b) and presence of dPEG6 (c, 1 pmol). The numbers represent the value of m/z.



Fig. S7 SNR (a) and Intensity (b) of LDI-TOF-MS signal peak (m/z = 305.3, $[M + Na]^+$) from dPEG6 of different concentrations based on Au@utSiO₂ CSNPs (18 nm Au core, 0.5 nM). The attenuation of laser intensity is 75 (black solid line) and 50 (red dot line), respectively.



Fig. S8 Intensity (a) and SNR (b) of LDI-TOF-MS signal peak (m/z = 305.3, $[M + Na]^+$) of dPEG6 (1 pmol) based on Au@SiO₂ CSNPs (18 nm Au core) with different thicknesses of silica shell and different concentrations; c) Intensity (black solid line) and SNR (green dash line) of LDI-TOF-MS signal peak (m/z = 305.3, $[M + Na]^+$) of dPEG6 (1 pmol) based on Au@utSiO₂ CSNPs (50 nm Au core); d) Intensity of LDI-TOF-MS signal peak (m/z = 305.3, $[M + Na]^+$) of dPEG6 (1 pmol) based on Au@utSiO₂ CSNPs (50 nm Au core); d) Intensity of LDI-TOF-MS signal peak (m/z = 305.3, $[M + Na]^+$) of dPEG6 (1 pmol) based on Au@utSiO₂ CSNPs (50 nm Au core); d) Intensity of LDI-TOF-MS signal peak (m/z = 305.3, $[M + Na]^+$) of dPEG6 (1 pmol) based on Au@utSiO₂ CSNPs with different size of Au core. The numbers in square parentheses represent the size of corresponding NPs (nm). Data points are the average of 5 parallel data. The vertical lines represent the variances of corresponding data.

OH OH O_2 ľ Η 1500 -174.1 a) 1000 152.1 (715)Intensity (a.u.) (8) 500 0 170 155 175 180 160 165 150 185 200 40 1 45 100 210.1 194.1 b) (30) 50 (9) 0 215 2Ò0 210 2Ż0 190 195 205 225 180 185 230m/z

4. LDI-TOF-MS spectra based on Au@utSiO₂ CSNPs

Fig. S9 The structure and LDI-TOF-MS of some small functional molecules based on Au@utSiO₂ CSNPs (18 nm Au core, 1 nM). The numbers represent the values of m/z and SNR (in the parentheses). The two marked peaks with an interval of 16 m/z are due to the cations of $[M + Na]^+$ and $[M + K]^+$, respectively. The peaks at m/z = 197.2 (marked with an asterisk) represent Au⁺ from gold core. a) N-(4-hydroxyphenyl)-acetamide, molecule 1, Mw = 151.2, 857 pmol; b) 2-(2-methyl-5-nitro-1H-imidazol-1-yl) ethanol, molecule 2, Mw = 171.2, 50 pmol.



Fig. S10 The structure and LDI-TOF-MS of some small functional molecules based on Au@utSiO₂ CSNPs (18 nm Au core, 1 nM). The numbers represent the values of m/z and SNR (in the parentheses). The two marked peaks with an interval of 16 m/z are due to the cations of $[M + Na]^+$ and $[M + K]^+$, respectively. a) Norfloxacin, molecule 1, Mw = 319.3, 50 pmol. There is a signal of $[M + H]^+$ cations at m/z=320.3; b) Amoxicillin, molecule 2, Mw = 365.5, 50 pmol. The peak at m/z=394.3 (marked with an asterisk) represents Au₂⁺ from gold core.



Fig. S11 The LDI-TOF-MS of roxithromycin (a, Mw = 837.0, 10 pmol) and β -cyclodextrin (b, Mw = 1135.0, 50 pmol) based on Au@utSiO₂ CSNPs (18 nm Au core, 1 nM). The numbers represent the value of m/z and SNR (in the parentheses). The two marked peaks with an interval of 16 m/z are due to the cations of $[M + Na]^+$ and $[M + K]^+$, respectively.



Fig. S12 The LDI-TOF-MS of NP30 based on CHCA (a) and Au@utSiO₂ CSNPs (b, 18 nm Au core, 1 nM). The amount of NP30 is 20 pmol (a) and 5 pmol (b), respectively. The marked peaks represent the peaks of maximum signal intensity, and the numbers show the value of m/z and SNR (in the parentheses).