Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Laser desorption/ionization on nanostructured-silicon: morphology matters

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1. The details of etching mechanisms

Both TSi and PSi substrates were prepared by one-step etching silicon without mask. The mechanism to produce TSi substrate is described as:

$Si + 4F \rightarrow SiF_4\uparrow$

Then the $Si^{\cdot}$, $F^{\cdot}$ and $O^{\cdot}$ form $Si_xO_yF_z$ passivates and accumulate on the silicon tip surface to mask.

$$xSi + yO + zF \rightarrow Si_xO_yF_z\uparrow$$

$$xSi + yO + zF \rightarrow Si_xO_yF_z\downarrow (self - mask)$$

The PSi substrate was prepared by Ag-assisted chemical etching. The mechanism is well accepted that the H_2O_2 is reduced at the metal:

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2h^+$$

Then the Si substrate is oxidized and dissolved:

$$Si + 4h^+ + 4HF \rightarrow SiF_4 + 4H^+$$

$$SiF_4 + 2HF \rightarrow H_2SiF_6$$

2. The detailed setup of the FDTD simulation

The angle of incident light (355 nm) was 15° in z-axis with the shape of plane wave. The mesh type was defined as auto non-uniform with min mesh step of 0.25 nm and the accuracy of the conformal mesh is 3. Monitor was placed in xz plane to image and plot the variation of E-field. The boundary condition was set as stretched coordinate perfectly matched layer (PML).

3. The relationship of rate coefficient (k(E)) and internal energy for $[4\text{-C-BP}]^+$

$k(E) = G^* (E - E_{act})/h\rho(E)$ (1)

The number of states, $G^{*}(E - E_{act})$, is in the range of E and E_{act} in transition state, and the density of states, $\rho(E)$, is at energy E; h is Planck's constant. The vibrational frequencies of the optimized geometries of 4-C-BP ion and the value of E_{act} (1.73 eV) were adopted from references.[1-3] The k(E) curve for the 4-C-BP ion as a function of internal energy is shown in Fig. S1, which was derived using Masskinetics Scientific Demo software33[4] (version 1.20; http://proteomics.ttk.mta.hu/ masskinetics/home/index.php) based on the Rice−Rampsberger−Kassel−Marcus (RRKM) statistical theory.[5]

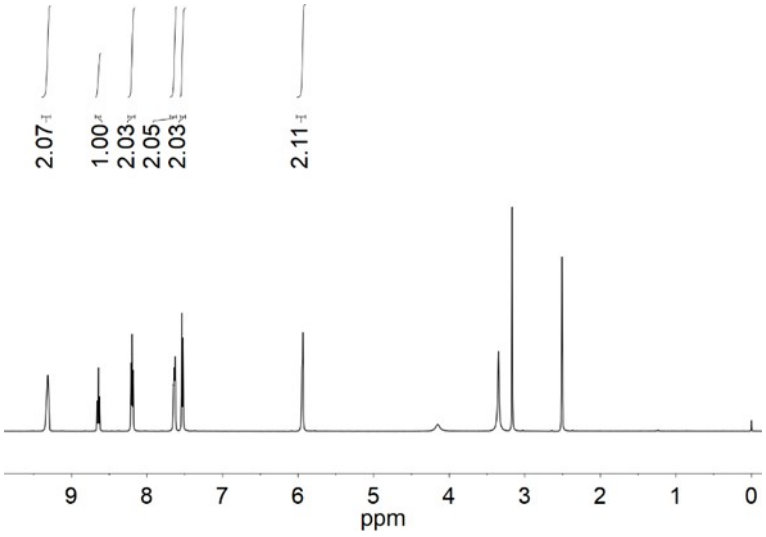

Fig. S1 ^{1}H NMR of the synthesized $[4\text{-C-BP}]^{+}$ chloride salt.

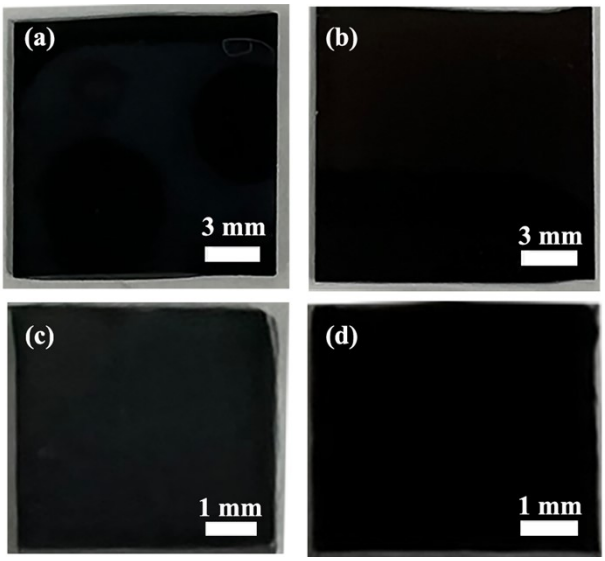

Fig. S2 Photographs of the (a, c) PSi-4 and (b, d) TSi-4 substrates.

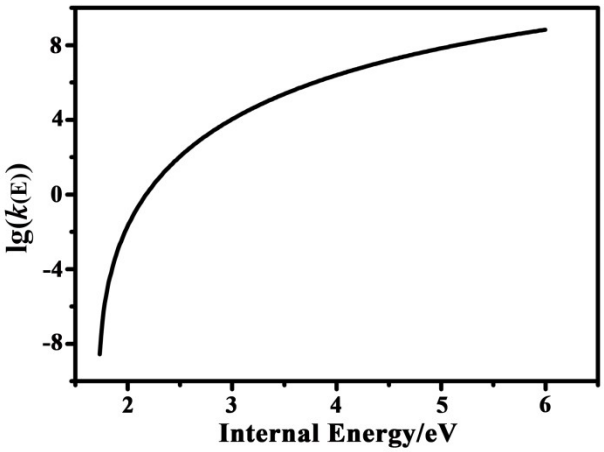

Fig. S3 The rate coefficient (k(E)) for [4-C-BP]$^+$ as a function of internal energy.

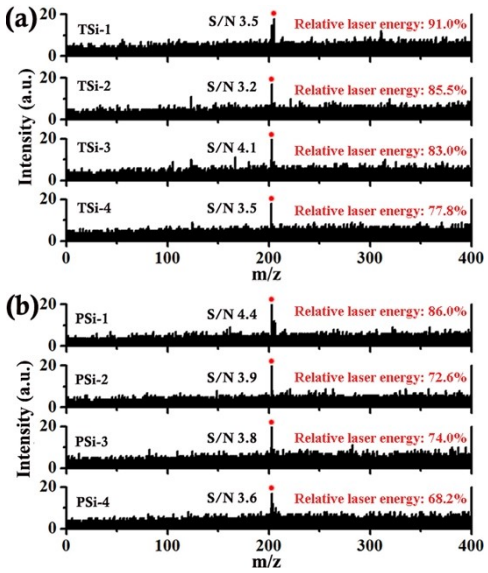

Fig. S4 SALDI-MS spectra of $[4\text{-C-BP}]^+$ detected at laser threshold on the (a) TSi (1–4) and the (b) PSi (1–4) substrates. The red-star-marked peaks at m/z 204 are from $[4\text{-C-BP}]^+$.

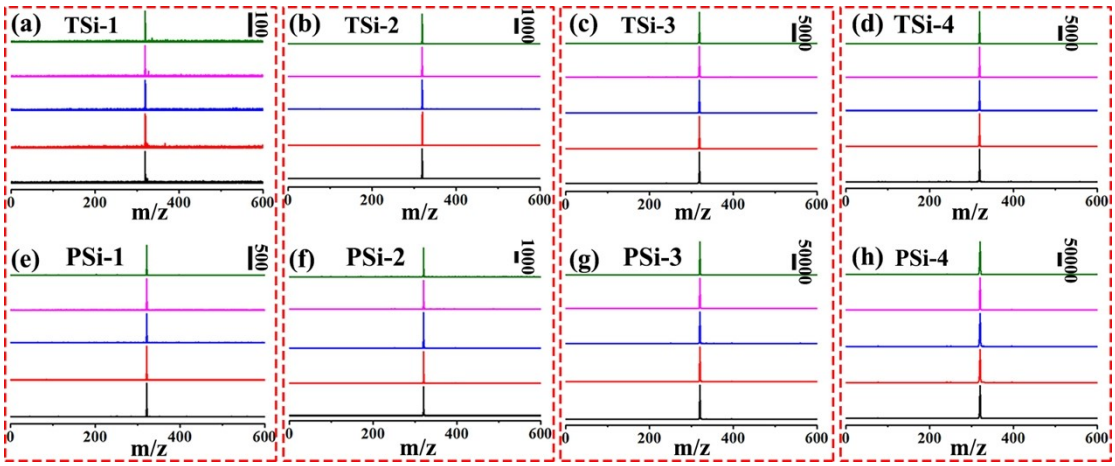

Fig. S5 SALDI-MS spectra of sodium tetraphenylborate obtained on the (a−d) TSi (1−4) and (e−h) PSi (1−4) substrates (different lines in each subgraph represent five replicate measurements).

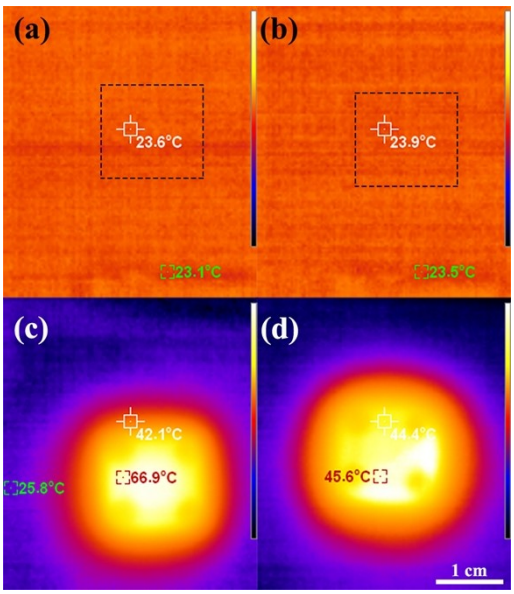

Fig. S6 Temperature distributions measured on PSi-4 substrate (a) before and (c) after excited by a mercury lamp; temperature distributions measured on TSi-4 substrate (b) before and (d) after excited by a mercury lamp.

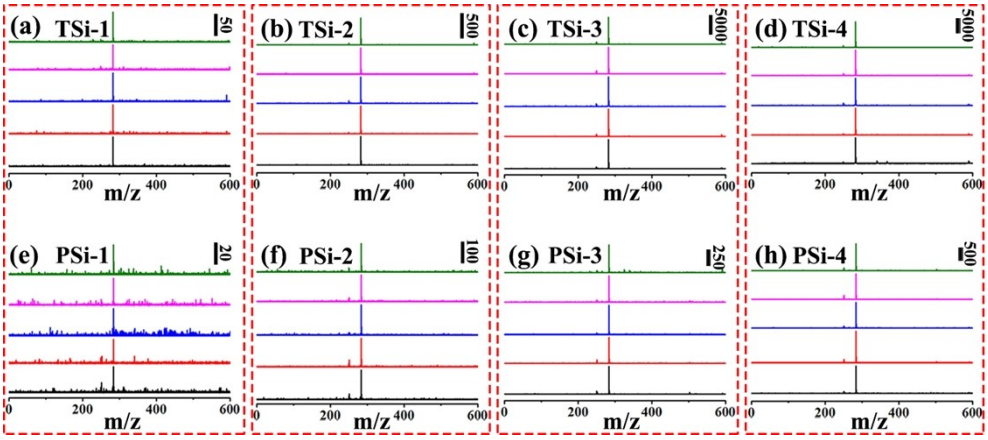

Fig. S7 SALDI-MS spectra of stearic acid obtained on the (a−d) TSi (1−4) and (e−h) PSi (1−4) substrates (different lines in each subgraph represent five replicate measurements).

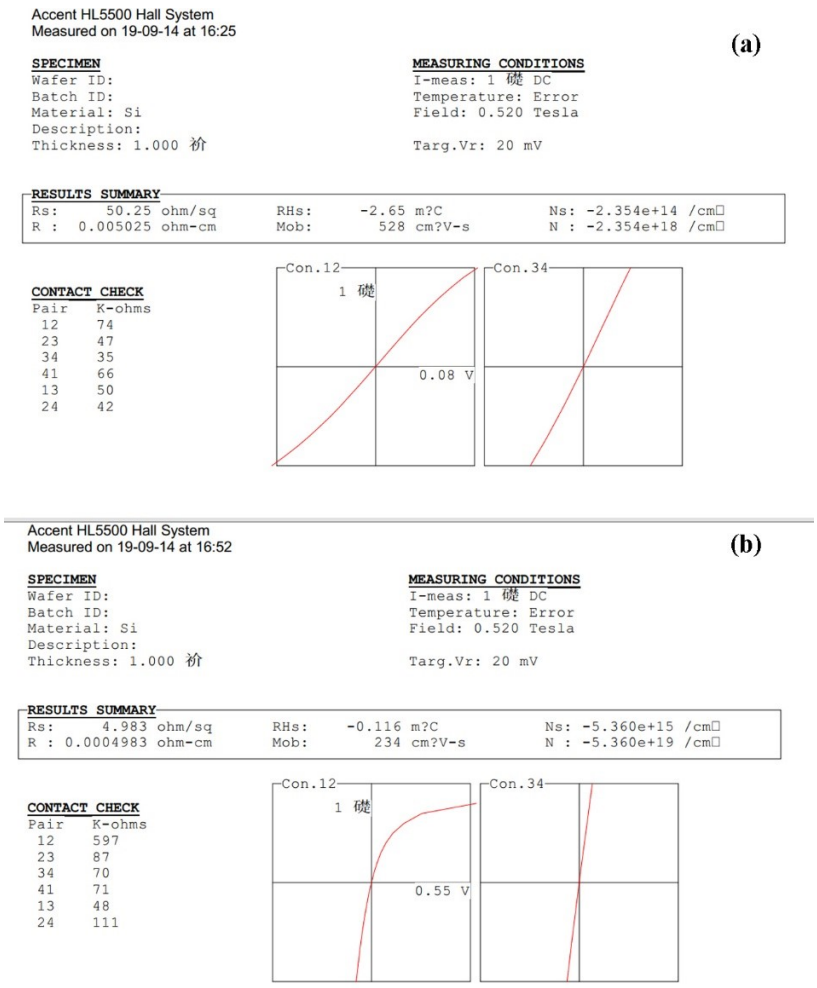

Fig. S8 The raw data for the electron mobility determination of (a) TSi-4 and (b)PSi-4.

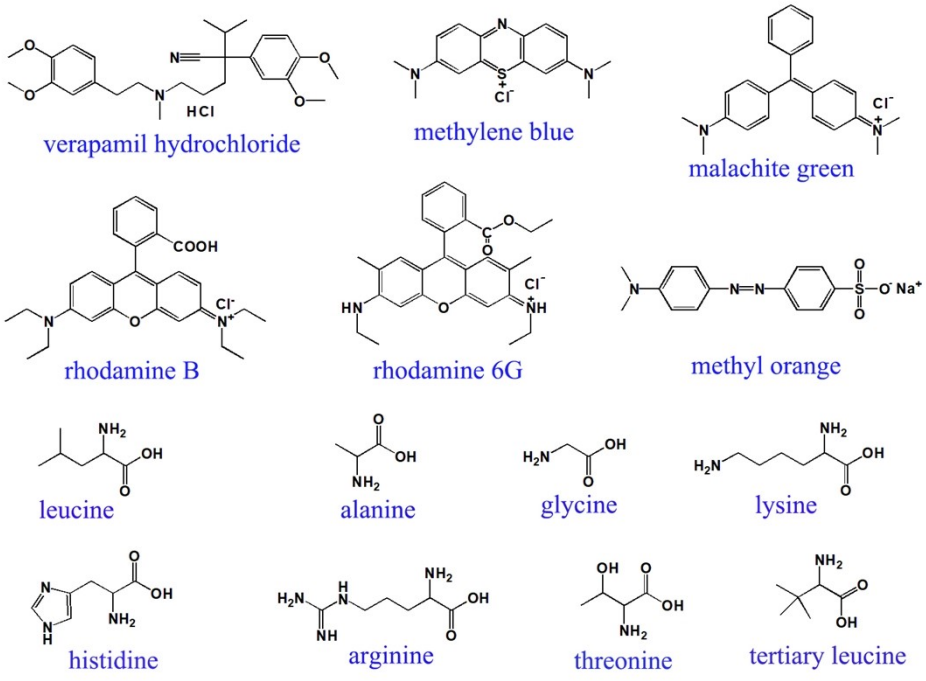

Fig. S9 Structures of analytes.

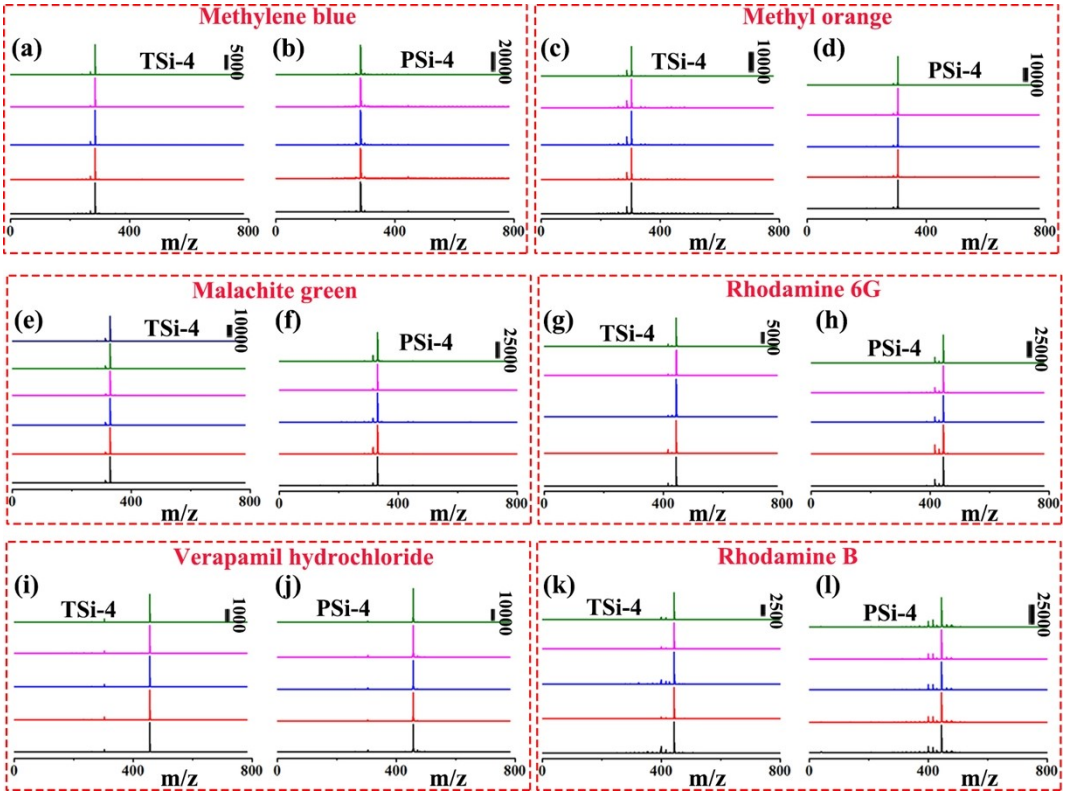

Fig. S10 SALDI-MS spectra of (a, b) methylene blue, (c, d) methyl orange, (e, f) malachite green, (g, h) rhodamine 6G, (i, j) verapamil hydrochloride, (k, l) rhodamine B obtained on the (a, c, e, g, i, k) TSi-4 and (b, d, f, h, j, l) PSi-4 substrates (different lines in each subgraph represent five replicate measurements).

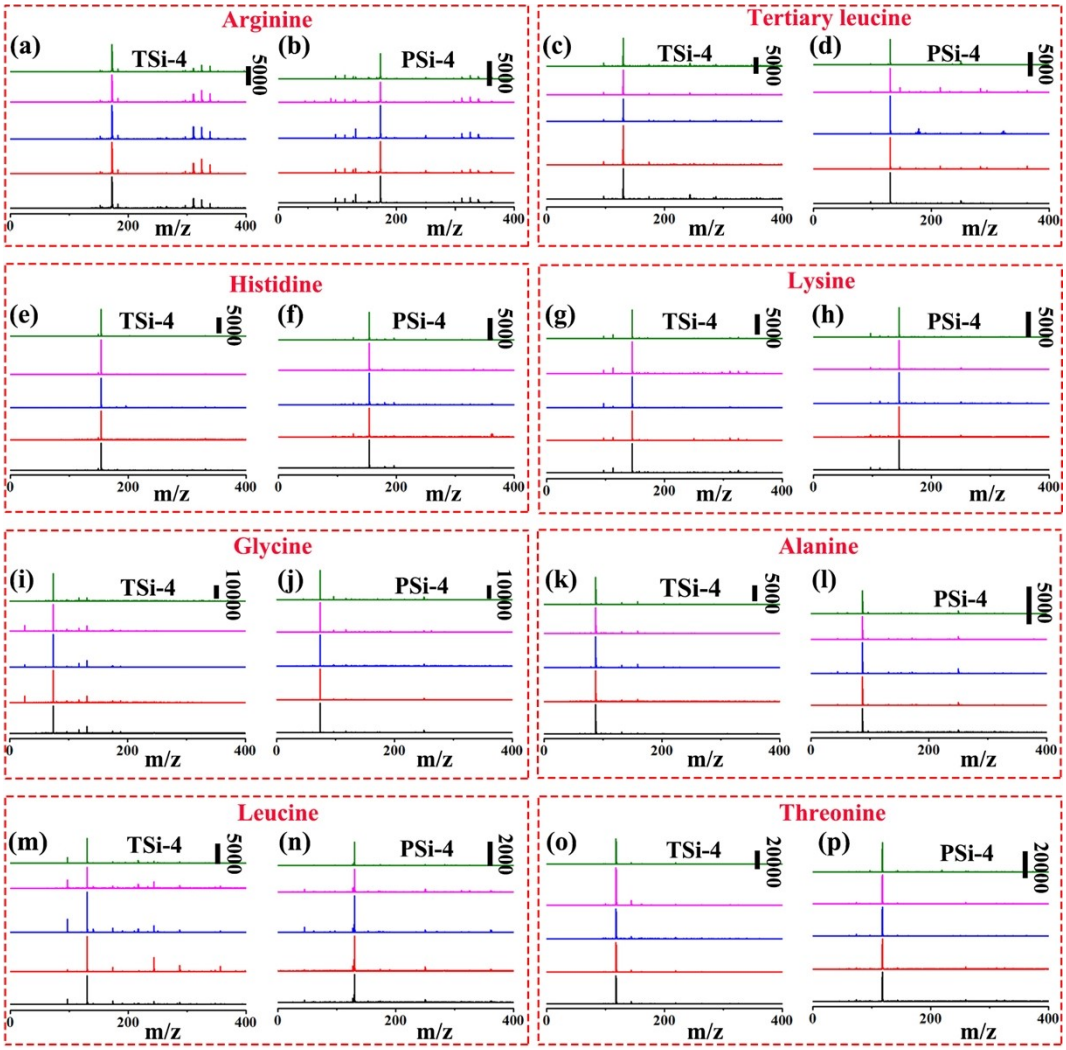

Fig. S11 SALDI-MS spectra of (a, b) arginine, (c, d) tertiary leucine, (e, f) histidine, (g, h) lysine, (i, j) glycine, (k, l) alanine, (m, n) leucine, (o, p) threonine obtained on the (a, c, e, g, i, k, m, o) TSi-4 and (b, d, f, h, j, l, n, p) PSi-4 substrates (different lines in each subgraph represent five replicate measurements).

Table S1. The etching time and corresponding total reflectivity of four pairs of TSi substrates.

	TSi-1	TSi-2	TSi-3	TSi-4
Etching time (min)	5	10	14	30
Absorbance	0.34	0.44	0.65	0.80

Table S2. Time of deposition Ag nanoparticles (AgNPs), etching time and corresponding total reflectivity of four pairs of PSi substrates.

	PSi-1	PSi-2	PSi-3	PSi-4
Time of deposition AgNPs (s)	103	15	15	15
Etching time (s)	120	5	70	90
Absorbance	0.37	0.47	0.69	0.85

Table S3. Structural parameters of the PSi substrates.

	PSi-1	PSi-2	PSi-3	PSi-4
pore size (nm)	35 ± 7	65 ± 12	90 ± 19	120 ± 28
pore depth (nm)	48 ± 18	210 ± 18	622 ± 25	1041 ± 44

Table S4. Structural parameters of the TSi substrates.

	TSi-1	TSi-2	TSi-3	TSi-4
height (nm)	30 ± 5	144 ± 9	330 ± 62	430 ± 28
bottom diameter (nm)	26 ± 7	66 ± 7	76 ± 13	82 ± 4
aspect ratio	1.15	2.18	4.34	5.24

References

1 G. Luo, I. Marginean and A. Vertes, *Anal. Chem.*, 2002, **74**, 6185−6190.

2 F. Derwa, E. de Pauw and P. Natalis, *Org. Mass Spectrom.*, 1991, **26**, 117−118.

3 C. Collette and E. de Pauw, *Rapid Commun. Mass Spectrom.*, 1998, **12**,165−170.

4 L. Drahos and K. Vekey, *J. Mass Spectrom.*, 2001, **36**, 237−263.

5 H. W. Tang, K. M. Ng, W. Lu and C. M. Che, *Anal. Chem.*, 2009, **81**, 4720−4729.