

## SUPPORTING INFORMATION

# Morphology Driven Control of Metabolite Selectivity using Nanostructure-initiator Mass Spectrometry

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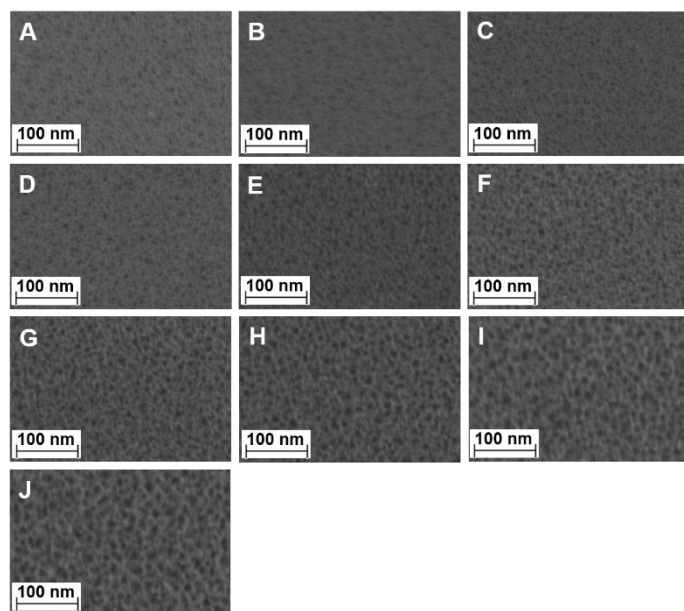
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## Table of Contents

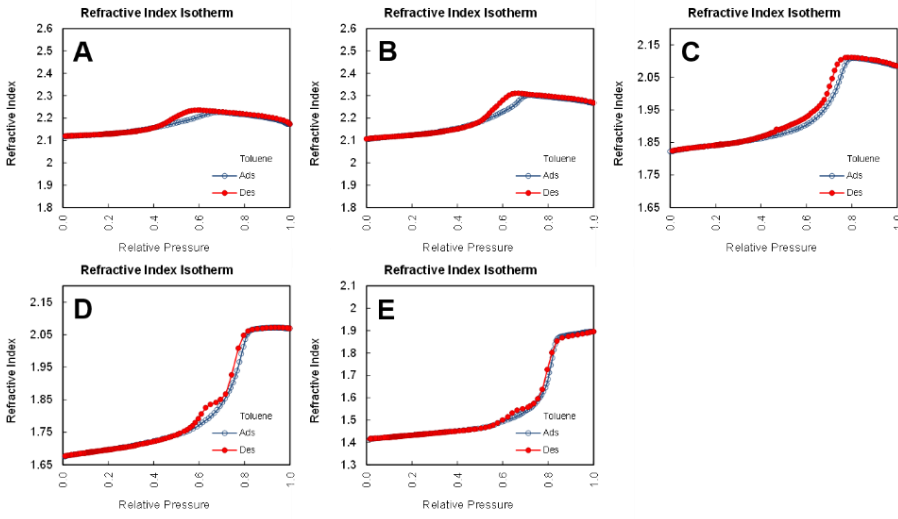
SI. Table 1. The corresponding molarities of the metabolites.....	S-3
SI. Fig. 1. SEM images of silicon surfaces obtained at variable etching time.....	S-3
SI. Fig. 2. Adsorption and desorption isotherms of toluene in these silicon surfaces.....	S-4
SI. Fig. 3. Pore size distributions of these silicon surfaces.....	S-4
SI. Fig. 4. The scatter plot of NIMS signal changes with the substrates' etching time.....	S-5
SI. Table 2. P-values calculated from single factor ANOVA and a post-hoc two sample t-test.....	S-5
SI. Fig. 5. Optimized geometries of the analytes calculated by Chem3D.....	S-6

**SI. Table 1. The corresponding molarities of the metabolites at 10 mg/L mass concentration.**

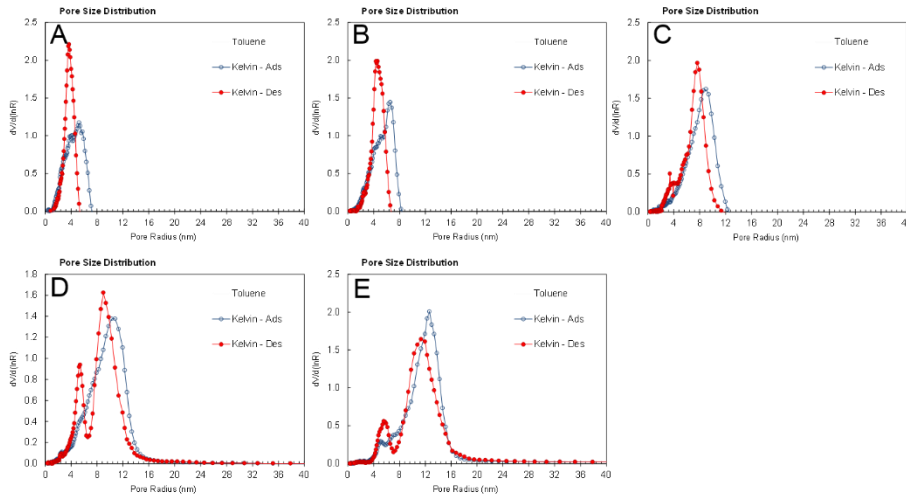
Metabolites	Concentration ( $\mu\text{M}$ )
Arginine	57.5
Palmitoylcarnitine	25.1
Streptomycin	17.2
Bradykinin	11.1
Angiotensin	7.7
Neurotensin	6.0
ACTH (clip 1-17)	4.8
ACTH (clip 18-39)	4.1
ACTH (clip 7-38)	2.7
Insulin B	2.9



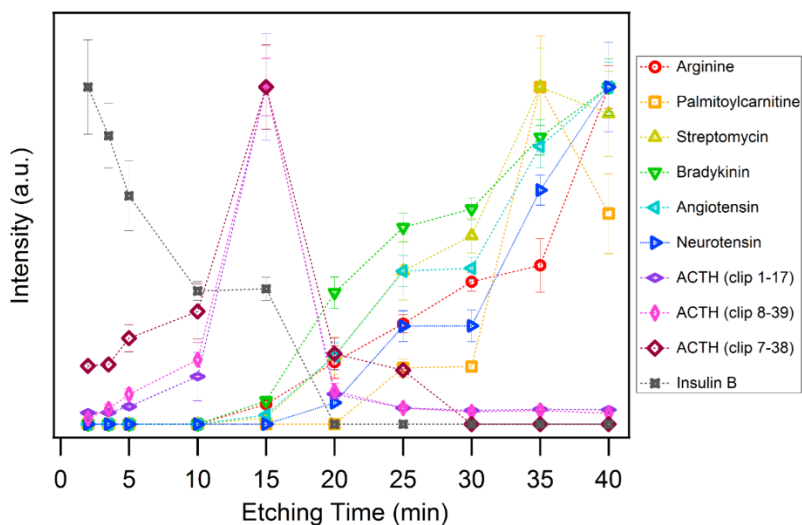
SI. Fig. 1. SEM images of silicon surfaces obtained at variable etching time: A. 2 mins; B. 3.5 mins; C. 5 mins; D. 10 mins; E. 15 mins; F. 20 mins; G. 25 mins; H. 30 mins; I. 35 mins; J. 40 mins.



SI. Fig. 2. Adsorption and desorption isotherms of toluene in silicon surfaces obtained at variable etching time: A. 2 mins; B. 10 mins; C. 20 mins; D. 30 mins; E. 40 mins.



SI. Fig. 3. Pore size distributions of silicon surfaces obtained at variable etching time: A. 2 mins; B. 10 mins; C. 20 mins; D. 30 mins; E. 40 mins.

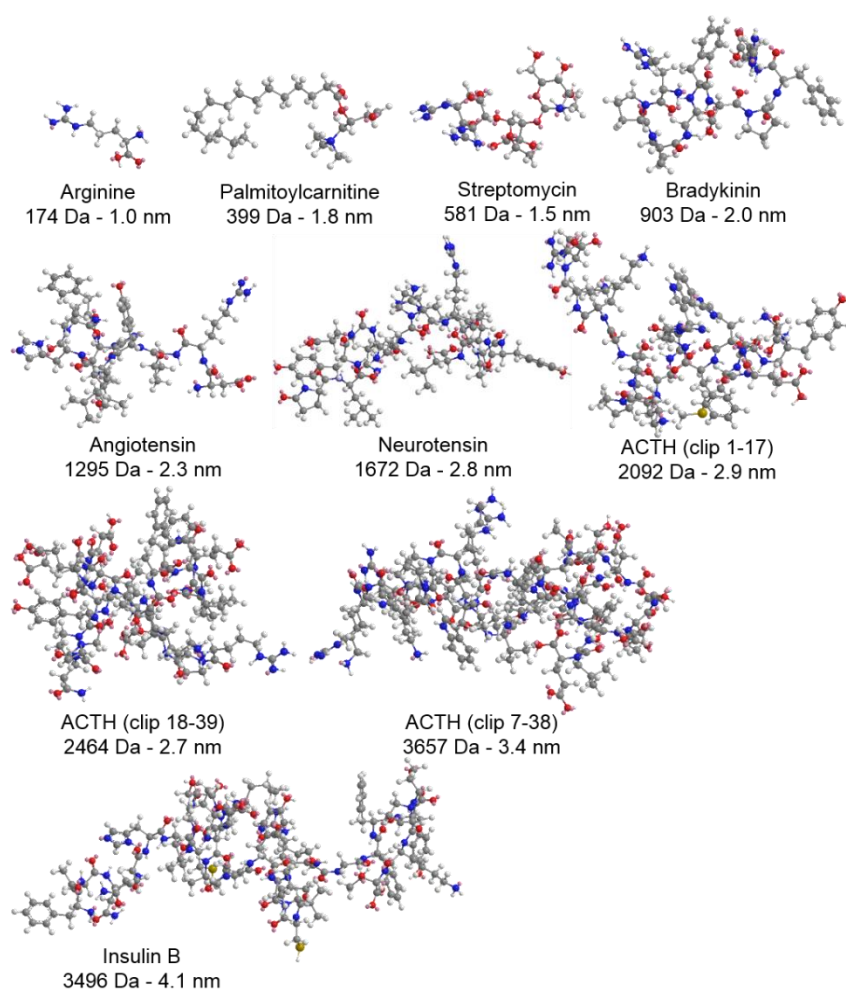


SI. Fig. 4. The scatter plot of NIMS signal changes with the substrates' etching time.

**SI. Table 2. P-values of different analytes' NIMS signals calculated from single factor ANOVA and a post-hoc two sample t-test (n=20).**

Source of Variation		P-value	Source of Variation		P-value
Arginine	Between Groups	1.17E-65	ACTH (clip 1-17)	Between Groups	1.22E-133
	15 min-20 min	8.15E-11		2 min-3.5 min	1.43E-01
	20 min-25 min	1.23E-10		3.5 min-5 min	1.30E-08
	25 min-30 min	3.22E-17		5 min-10 min	1.08E-05
	30 min-35 min	8.31E-03		10 min-15 min	3.93E-19
	35 min-40 min	8.34E-16		15 min-20 min	1.61E-16
Palmitoylcarnitine	Between Groups	1.23E-35		20 min-25 min	1.51E-14
	25 min-30 min	2.71E-01		25 min-30 min	1.30E-03
	30 min-35 min	1.67E-08		30 min-35 min	1.93E-04
	35 min-40 min	5.15E-06		35 min-40 min	8.67E-02
Streptomycin	Between Groups	8.31E-72	ACTH (clip 8-39)	Between Groups	1.51E-174
	15 min-20 min	1.73E-12		2 min-3.5 min	1.97E-08
	20 min-25 min	1.07E-12		3.5 min-5 min	1.24E-10
	25 min-30 min	3.08E-05		5 min-10 min	8.33E-09
	30 min-35 min	5.09E-15		10 min-15 min	2.78E-27
	35 min-40 min	2.18E-02		15 min-20 min	1.42E-23
Bradykinin	Between Groups	7.77E-89		20 min-25 min	2.33E-09
	15 min-20 min	5.16E-20		25 min-30 min	6.87E-09
	20 min-25 min	1.79E-16		30 min-35 min	1.84E-03
	25 min-30 min	2.79E-05		35 min-40 min	1.85E-06
	30 min-35 min	1.30E-16	ACTH (clip 7-38)	Between Groups	1.24E-87
	35 min-40 min	8.02E-08		2 min-3.5 min	1.78E-01

Angiotensin	Between Groups	2.00E-95	Insulin B	3.5 min-5 min	1.22E-08
	15 min-20 min	2.14E-14		5 min-10 min	2.86E-04
	20 min-25 min	1.21E-20		10 min-15 min	2.69E-20
	25 min-30 min	2.59E-01		15 min-20 min	1.37E-19
	30 min-35 min	7.00E-20		20 min-25 min	9.28E-05
	35 min-40 min	5.13E-10		Between Groups	5.09E-43
Neurotensin	Between Groups	4.74E-66	2 min-3.5 min	2.86E-04	
	20 min-25 min	9.33E-16	3.5 min-5 min	8.25E-07	
	25 min-30 min	4.68E-01	5 min-10 min	2.70E-11	
	30 min-35 min	3.76E-27	10 min-15 min	2.56E-01	
	35 min-40 min	5.68E-10			



SI. Fig. 5. Optimized geometries of the analytes calculated by Chem3D, and their molecular lengths measured from the longest sides.