# Peptide Sequencing with Top-down Synthesized $TiO_2$ Nanowires Using Laser Desorption/Ionization Time-of-Flight Mass Spectrometry

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The Association for Mass Spectrometry: Applications to the Clinical Lab

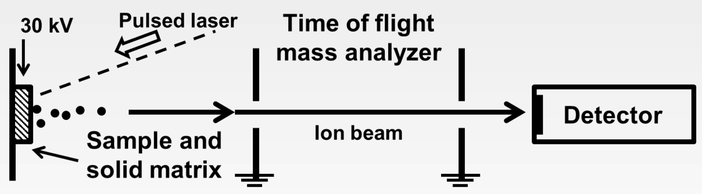
## Introductions

• **Objective**

**Synthesis and apply $TiO_2$ nanowire target chip to LDI-TOF mass spectrometry for peptide sequencing**

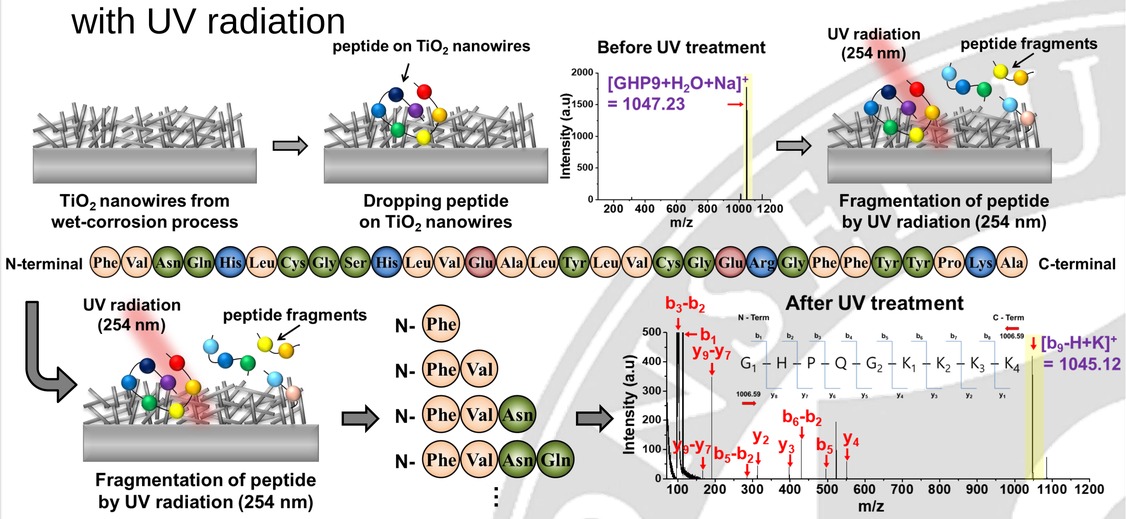
• **Laser desorption/ionization time-of-flight (LDI-TOF)**

- Advantages:
Short analysis time,
high sensitivity,
low sample consumption




• **Peptide sequencing using $TiO_2$ nanowire chip**

- Fragmentation of a peptide by photocatalytic decomposition with UV radiation

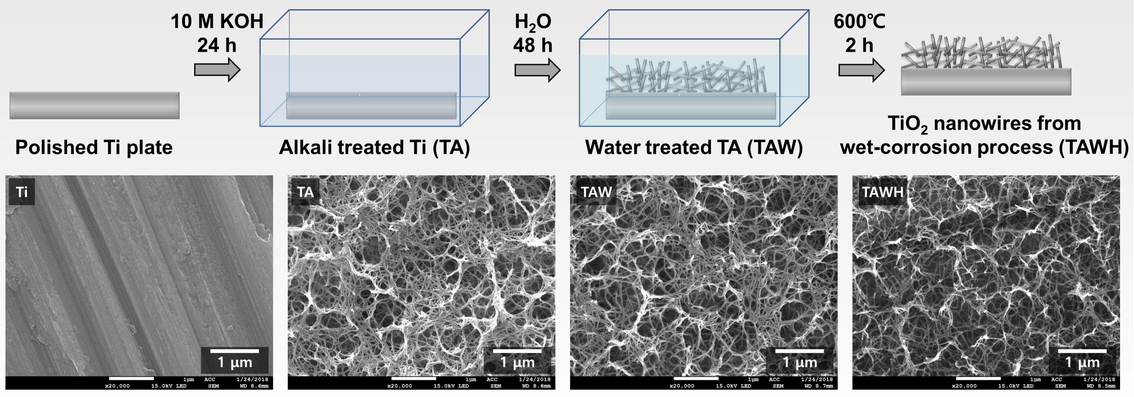



➡ **$TiO_2$ NW with photocatalytic activity was used to peptide sequencing**

## Characterization and Optimization

• **Synthesis of $TiO_2$ nanowire target chip**

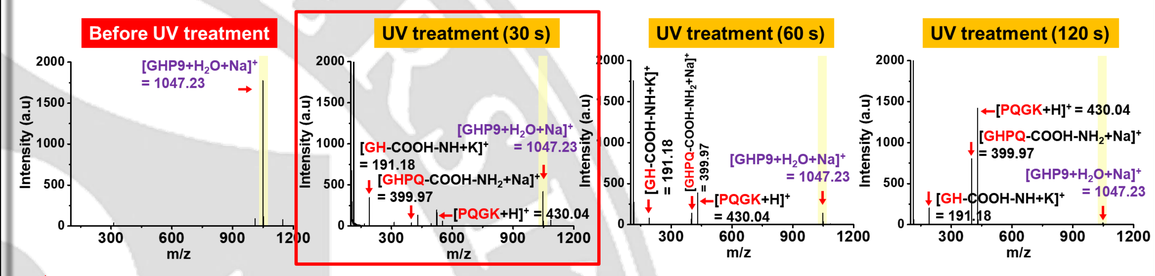
- Synthesis by mild hydrothermal (wet-corrosion) process
- Porous structure was generated after alkali treatment




< $TiO_2$ nanowire synthesis process and SEM images of each process >

• **Optimization of UV radiation time for fragmentation**

- GHP9 (GHPQGKKKK) peptide was fragmented on $TiO_2$ nanowire plate with UV for different exposure time (30, 60, 120 s)



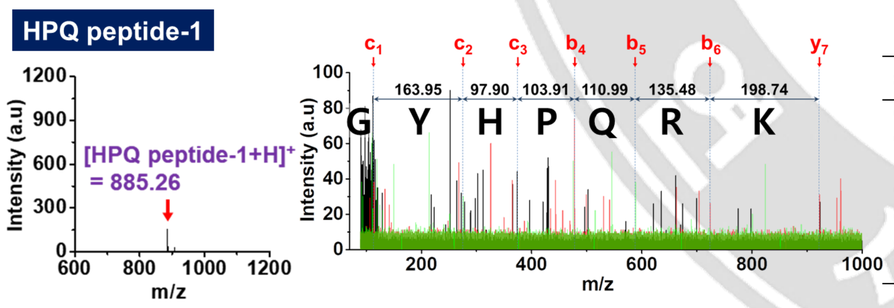

➡ **Optimized UV exposure time for sequencing was determined to 30 sec**

## Peptide sequencing using $TiO_2$ nanowire target chip

• **Peptide sequencing using $TiO_2$ nanowire chip**

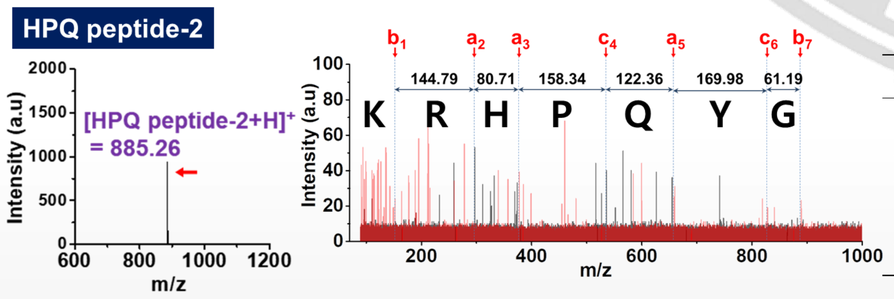
- Peptide fragment ions obtained by UV radiation with $TiO_2$ nanowire
- The fragment ions were assigned to a, b, c (from N-terminal) and x, y, z (from C-terminal) form
- Three different peptides with same molecular weight (884.45 Da)

**HPQ peptide-1**



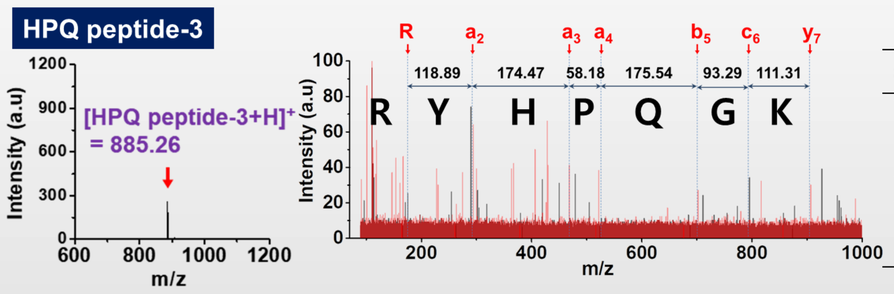

| Sequence | Observed *m/z* monoisotropic | Expected ion form* |
|---|---|---|
| GYHPQRK | 923.14 | $[GYHPQRK+K]^+$ |
| GYHPQR | 724.40 | $[(GYHPQR-OH)-NH_2+H]^+$ |
| GYHPQ | 588.92 | $[(GYHPQ-OH)-NH_2-H+Na]^+$ |
| GYHP | 477.92 | $[(GYHP-OH)+Na]^+$ |
| GYH | 374.02 | $[(GYH-OH+NH_3)-H]^{+\cdot}$ |
| GY | 276.11 | $[(GY-OH+NH_3)-H+K]^+$ |
| G | 112.16 | $[(G-OH+NH_3)-2H+K]^{+\cdot}$ |

**HPQ peptide-2**




| Sequence | Observed *m/z* monoisotropic | Expected ion form* |
|---|---|---|
| KRHPQYG | 889.82 | $[(KRHPQYG-OH)+Na]^+$ |
| KRHPQY | 828.63 | $[(KRHPQY-OH+NH_3)]^+$ |
| KRHPQ | 658.65 | $[(KRHPQ-COOH)+K]^+$ |
| KRHP | 536.29 | $[(KRHP-OH+NH_3)]^+$ |
| KRH | 377.96 | $[(KRH-COOH)-NH_2]^{+\cdot}$ |
| KR | 297.25 | $[(KR-COOH)+H+K]^+$ |
| K | 152.46 | $[(K-OH)+Na]^+$ |

**HPQ peptide-3**



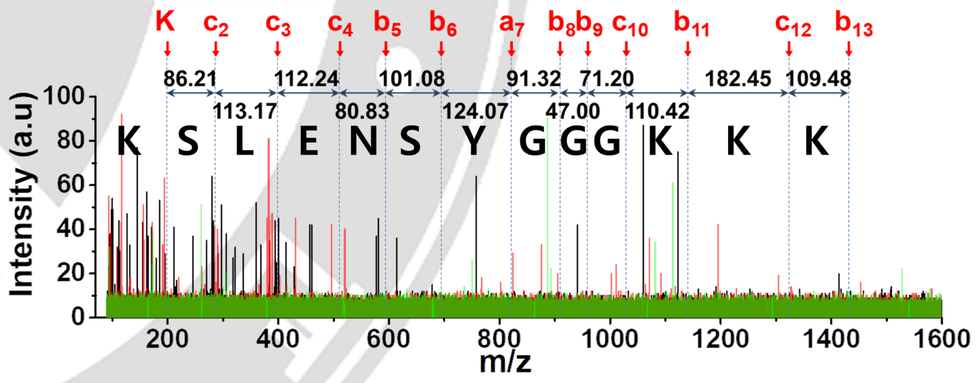

| Sequence | Observed *m/z* monoisotropic | Expected ion form* |
|---|---|---|
| RYHPQGK | 907.04 | $[RYHPQGK+Na]^+$ |
| RYHPQG | 795.73 | $[(RYHPQG-OH+NH_3)+K]^+$ |
| RYHPQ | 702.45 | $[(RYHPQ-OH)-H_2O-H+K]^+$ |
| RYHP | 526.90 | $[(RYHP-COOH)+H]^+$ |
| RYH | 468.72 | $[(RYH-COOH)+K]^+$ |
| RY | 294.25 | $[(RY-COO)+H]^+$ |
| R | 175.37 | $[R+H]^+$ |

< Before UV treatment > < After UV treatment > < Amino acid sequencing >

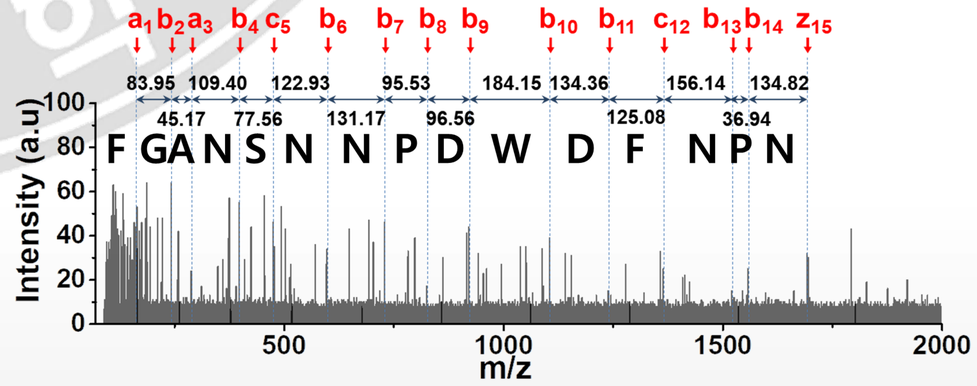
➡ **Sequences of three different HPQ peptides were completely determined**

- Peptide sequencing from mass peaks of multiple spectra

**BPA-1 peptide (n=3)**




**PreS1 peptide (n=1)**




➡ **Peptide sequences were determined from multiple LDI-TOF spectra**

• **Conclusions**

- $TiO_2$ nanowire target chip with photocatalytic activity was prepared using wet-corrosion process
- Amino acid sequences of three different peptides with same molecular weight were clearly analyzed
- GHP9, BPA-1, PreS1 peptide were analyzed from mass peaks from single or three LDI-TOF MS spectra

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