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Identification and Semi-Quantification of Porphyrin-Silica Composite Nanoparticles Using Atmospheric Solids Analysis Probe Mass Spectrometry

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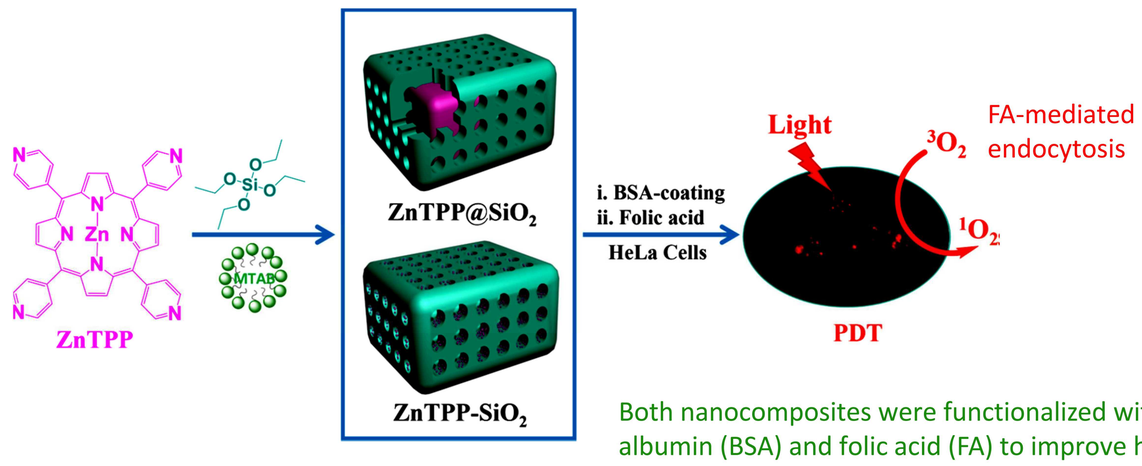
Introduction

Porphyrins are vital pigments involved in biological energy transduction processes. Their abilities to absorb light, then convert it to energy, have raised the interest of using porphyrin nanoparticles as photo-sensitizers in photodynamic therapy (PDT). A recent study showed that self-assembled porphyrin-silica composite nanoparticles can selectively destroy tumor cells, but detection of the cellular uptake of porphyrin-silica composite nanoparticles was limited to imaging microscopy. Atmospheric Solids Analysis Probe-Mass Spectrometry (ASAP-MS) can generate ions at ambient pressure and collect mass spectra with minimal pre-treatment for solid and liquid samples. Here we developed a novel method to rapidly identify and semi-quantify porphyrin-silica composite nanoparticles using ASAP-MS.

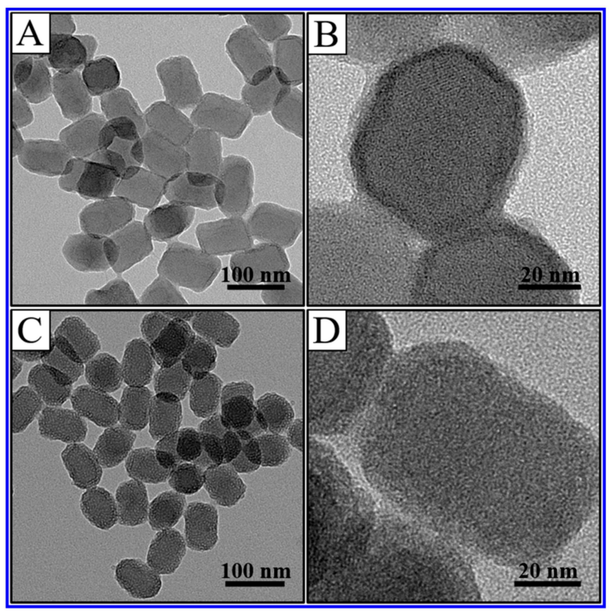
Controlled Self-Assembly of Core-Shell Structured ZnTPP@SiO_2 and Solid ZnTPP-SiO_2 Nanocomposite Particles that function as tumor cell photosensitizer



Both nanocomposites were functionalized with bovine serum albumin (BSA) and folic acid (FA) to improve hydrophilicity and cancer cell targeting efficacy.

J. Wang *et al*. *Nano Lett*. 2017, 17, 6916-6921.

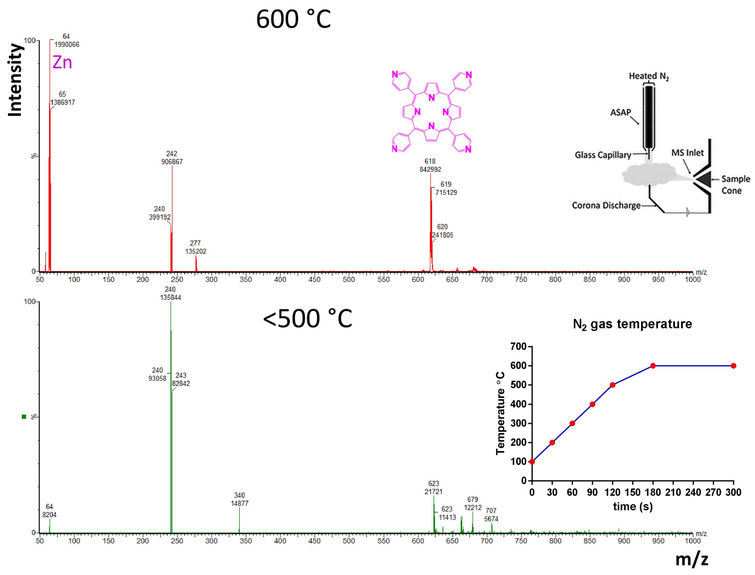
Porphyrin-Silica Nanocomposite Particles



Porphyrin-silica nanocomposite particles self-assemble through noncovalent interactions of ZnTPP within surfactant micelles. A and B: Core-shell structured ZnTPP@SiO_2. C and D: Solid ZnTPP-SiO_2.

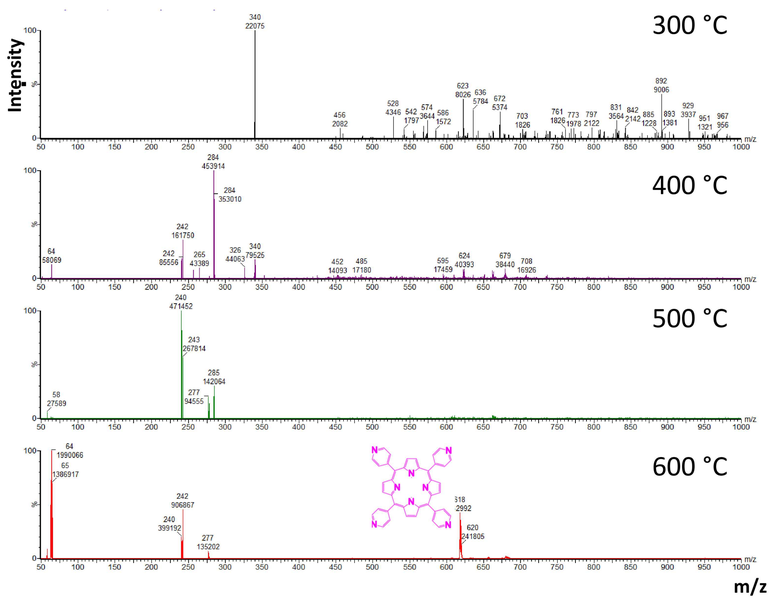
J. Wang *et al*. *Nano Lett.* 2017, 17, 6916-6921.

ASAP-MS fingerprint of ZnTPP



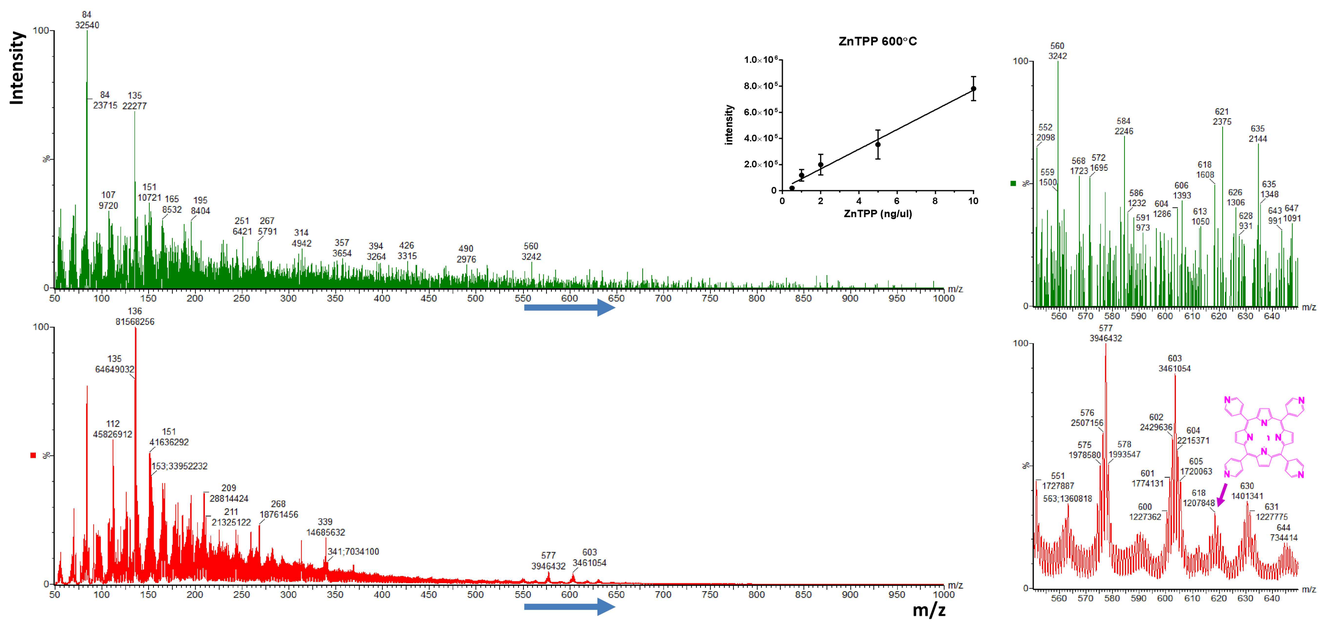
Samples were attached to the ASAP glass probe by drying 10 µl of each solution. Sample ionization and mass detection were achieved by increasing N_2 gas temperature from 100 to 600 °C. ZnTPP fingerprint mass spectrum was detected at 600 °C. The mass spectra presented were averaged from more than 100 scans.

ASAP-MS Temperature-Mass Spectra Profiles of ZnTPP



Temperature-mass spectra profiles of ZnTPP starting at 300 °C (ZnTPP melting point). Zn started dissociating at 400 °C, and ZnTPP signature peak was only detected at 600 °C. ASAP allows ionization and transportation of high-mass molecules to MS inlet as gas-phase ions. The product pattern was preserved by no condensation within a short diffusion length.

ASAP-MS identification and semi-quantification of ZnTPP in HeLa cells



HeLa cells were cultured on 12 well plates to 95 % confluency. 8 µM of porphyrin-silica nanocomposite particles were added into culture media, and incubated for 2 h. Cells were washed with ice-cold phosphate buffered saline (PBS) for three times, then resuspended into 70 % ethanol and loaded onto ASAP probe. Following the same N_2 gas temperature profile, cellular accumulation of ZnTPP was detected at 600 °C. The mass spectra presented were averaged from more than 100 scans.

Conclusions

Assuming similar ionization and detection efficiency under same MS condition, standard curves with known concentrations of ZnTPP standards can be generated and ZnTPP cellular accumulation amount can be quantified. Treated cells can be loaded onto ASAP probe directly without the need of sample preparation. Therefore, ASAP-MS provides a rapid method to identify and semi-quantify the cellular accumulation of Porphyrin-silica nanocomposite particles. This study established a quantification toolset for porphyrin nanoparticles.

Acknowledgement

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