Supporting Information

One-step encapsulation, storage and controlled release of small molecular weight organic compounds *via* electroplated nanoparticles

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Methods:

H_2PdCl_4, $(NH_4)_2HPO_4$ and $Na_2HPO_4 \cdot 12H_2O$ used in nanoparticles synthesis were of 99 % purity (Sigma Aldrich), HCI (37%, ICP-Ms quality) was obtained from Honeywell Fluka (Germany). The MALDI matrices, *viz.* α-cyano-4-hydroxycinnamic acid (CHCA), α-cyano-2,3,4,5,6-pentafluorocinnamic acid (FCCA) and polished steel target (MTP 384 type) were purchased from Bruker Daltonik Gmbh (Germany). Reserpine was obtained from Sigma-Aldrich (Steinheim, Germany); acetonitrile and methanol were from Merck (Darmstadt, Germany). All other chemicals were purchased from Sigma-Aldrich (97-99% purity). All the solvents were of HPLC quality. Organic-free, deionized water was generated by an Elga PureLab (Celle, Germany) water purification system.

MALDI matrices preparation

Standard MALDI experiments were performed using the drying droplet method by mixing equal amounts of analyte and matrix solutions (5 mg/mL in 50:50 [v/v] in water: acetonitrile). Analyte solutions (1 μL) were spotted directly onto the electroplated targets and spots dried under ambient conditions.

Electroplating experiment

The synthesis of Pd-NPs with standard MALDI matrices electrochemically bound to the steel target was conducted by electroplating from Pd-polyelectrolyte (pH=4.5-5) with CHCA or FCCA (2500 ppm) at room temperature 20±2°C, directly over the steel plates. Electrolysis was performed using a VMP 3 (Biologic SAS, Claix, France) potentiostat. The following parameters were used: I_k, 10 mA/dm^2 to 100 mA/dm^2, t_{el} from 30 sec to 3 min, Pd anode (99.9 %).

Scanning Electron Microscopy (SEM)

SEM images were captured on a Quanta (Hillsboro, OR, USA) 400 FEG system equipped with an EDAX (Mahwah, NJ, USA) Genesis V 6.04 X-ray spectral analysis system, at an accelerating voltage of 10 keV. The image size was 1024x884 pixels.

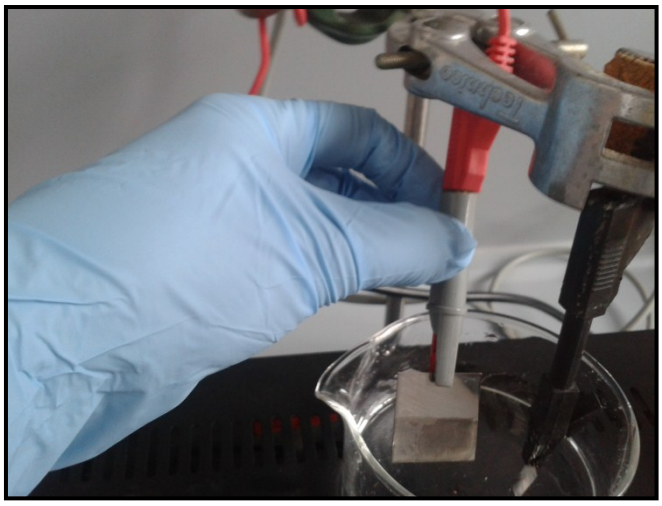
HPLC analysis and Mass Spectrometry

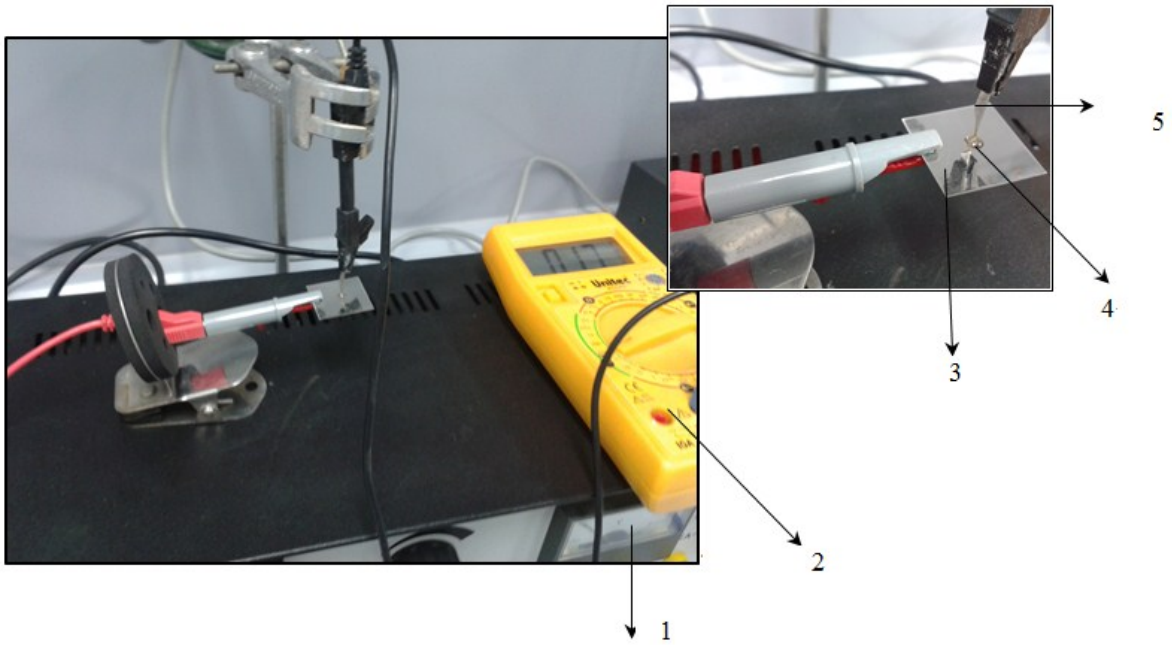
The HPLC analysis was performed on an Agilent Infinity 1260 series instrument (Agilent Technologies, CA, USA) coupled with a quadrupole time-of-flight mass spectrometer Q-TOF LC/MS 6545 (Agilent Technologies, CA, USA) equipped with Jet Stream Thermal Focusing Technology ESI source. For elution experiment, a droplet of 10 µl of ACN:H_2O (50:50, *v/v*) preliminary spotted for 5 min onto the hybrid plates, was taken for subsequent LC-MS analysis. Chromatographic separation was achieved on the ZORBAX Eclipse Plus C18 column (2.1×50 mm, particles size 1.8 µm) (Agilent, CA, USA). The mobile phase consisting of ACN (Solvent A) and 0.3% formic acid (FA) in water (Solvent B) and was used in the following gradient elution step: 10% Solvent A, was held for 2 min, then increased to 90% in 3 min and held for 2 min, and returned back to the starting conditions in 2 min. The column operation temperature was fixed at 30 ºC, the mobile phase flow rate was 300 µl/min and the injection volume was 1 µL. MS scans were recorded in a negative ion mode, operating under capillary voltage at 4500 V; the fragmentor voltage was set at 30 eV; dry gas temperature at 350 ºC; gas flow at 9 L/min; nebulizing gas pressure at 45 psi. To monitor a leakage of CHCA and FCCA after elution experiment from the hybrid plates, mass spectra at *m/z* 100-500 were recorded. The data acquisition was controlled by MassHunter Software Tool.

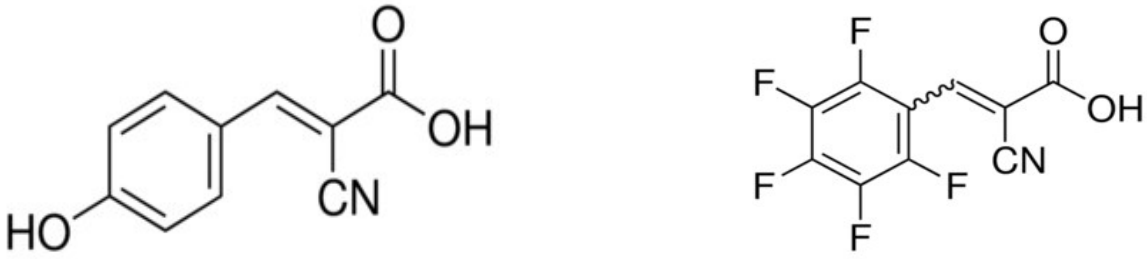
MALDI/LDI experiments were performed on a Bruker Esquire 3000+ESI-ion trap MS (Bruker Daltonics, Bremen, Germany) operated by Bruker esquire control 5.3 software equipped with atmospheric pressure (AP)-MALDI ion source and Nd:YAG solid-state laser (355 nm). Mass spectra were recorded in positive ion full-scan mode from *m/z* 100-700.

Monitoring co-deposition of small molecular weight organic compounds using QCM system

The synthesis reproducibility of hybrid targets were estimated in a droplet by means of quartz crystal microbalance (QCM) measurement system. QCM quartz crystals (AT-cut, diameter 14 mm, surface area 1.54 cm^2) with a basic frequency of 10 MHz and software "NanoSens Explorer" were provided by Ltd "Sensors and New technology" (SNT, Voronezh, Russia). The temperature within the experiments was maintained at 20±2 C. Frequency shifts represent weight of co-deposited organic-inorganic hybrid structures with nanogram precision. The mass of the co-deposited hybrid structures was estimated using *Sauerbrey* equation [22].







A) B)

Figure S1. (*top*) – laboratory settings for the hybrid MALDI/LDI co-deposion in bulk; (*middle*) – co-deposion in droplet: 1 – potentiostat; 2 – digital multimeter (DMM); 3 – polished steel plate; 4 – 10 µl of Pd-electrolyte doped with MALDI matrces; 5 – Pd-wires/electrode; (*bottom*) – chemical structure of the tested MALDI-matrices: A) α-Cyano-4-hydroxycinnamic acid (CHCA), 189.17 g/mol; B) α-Cyano-2,3,4,5,6-pentafluorocinnamic acid (FCCA), 263.12 g/mol.

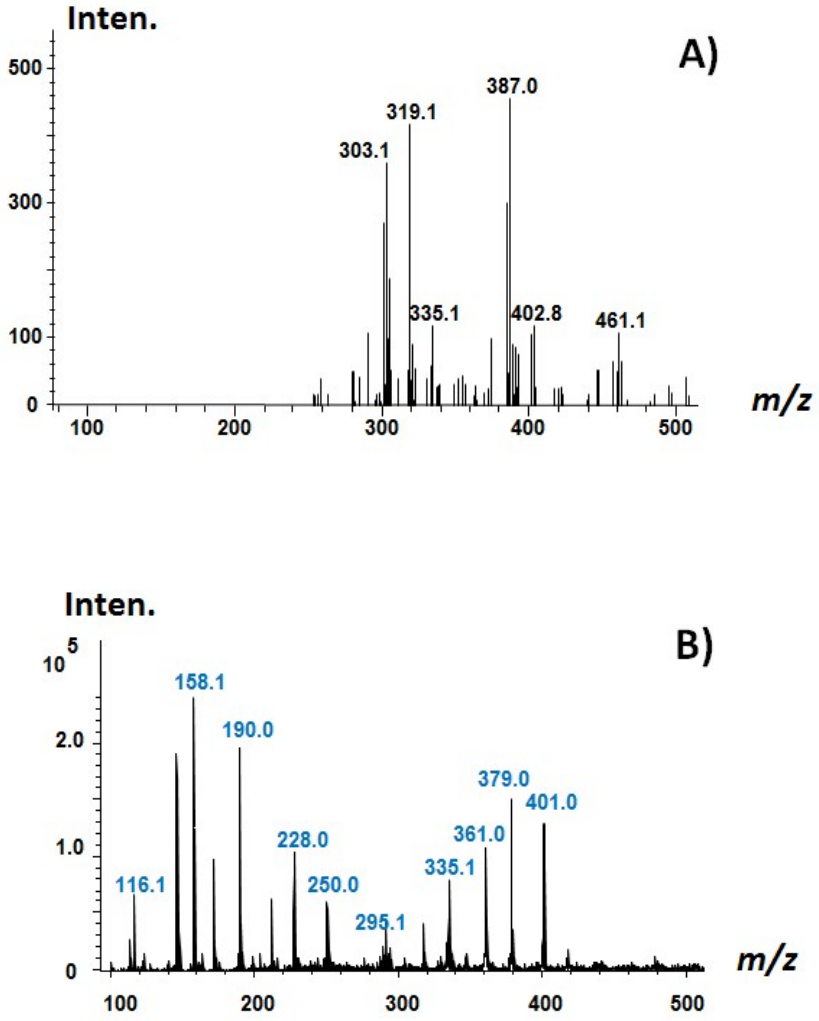


Figure S2. TIC-mass spectra obtained in positive detection mode (before pipetting of analytes) from the hybrid MALDI/LDI targets (*shown for encapsulated CHCA as a case study*) prepared at the same deposition time of 30 sec and different currents: **A**) 100 mA: **B**) 10 mA.

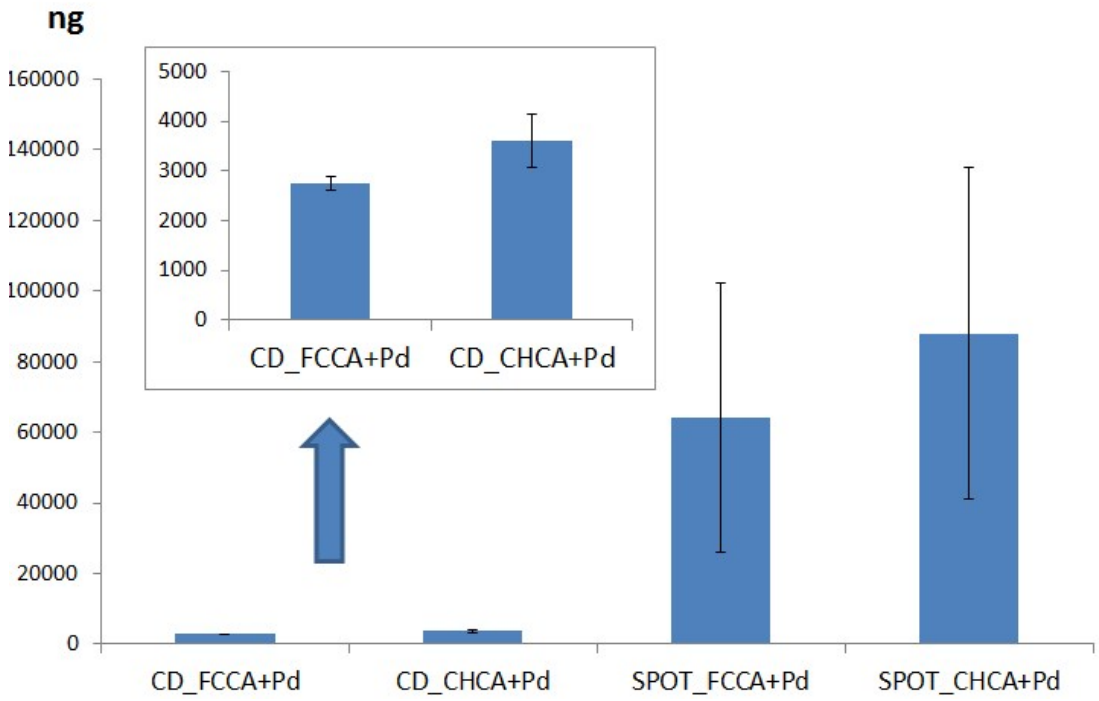


Figure S3. Estimation of the deposited rates (t = 20±2 °C) of MALDI/LDI hybrids in CD and SPOT methods by QCM measurements using *Sauerbrey* model [22]. The bars represent the mean ±SD of experiments (n = 7). NOTE: 10 µl of polyelectrolyte was spotted onto QCM in CD and 1 µl in SPOT method to avoid overloading of microbalances.

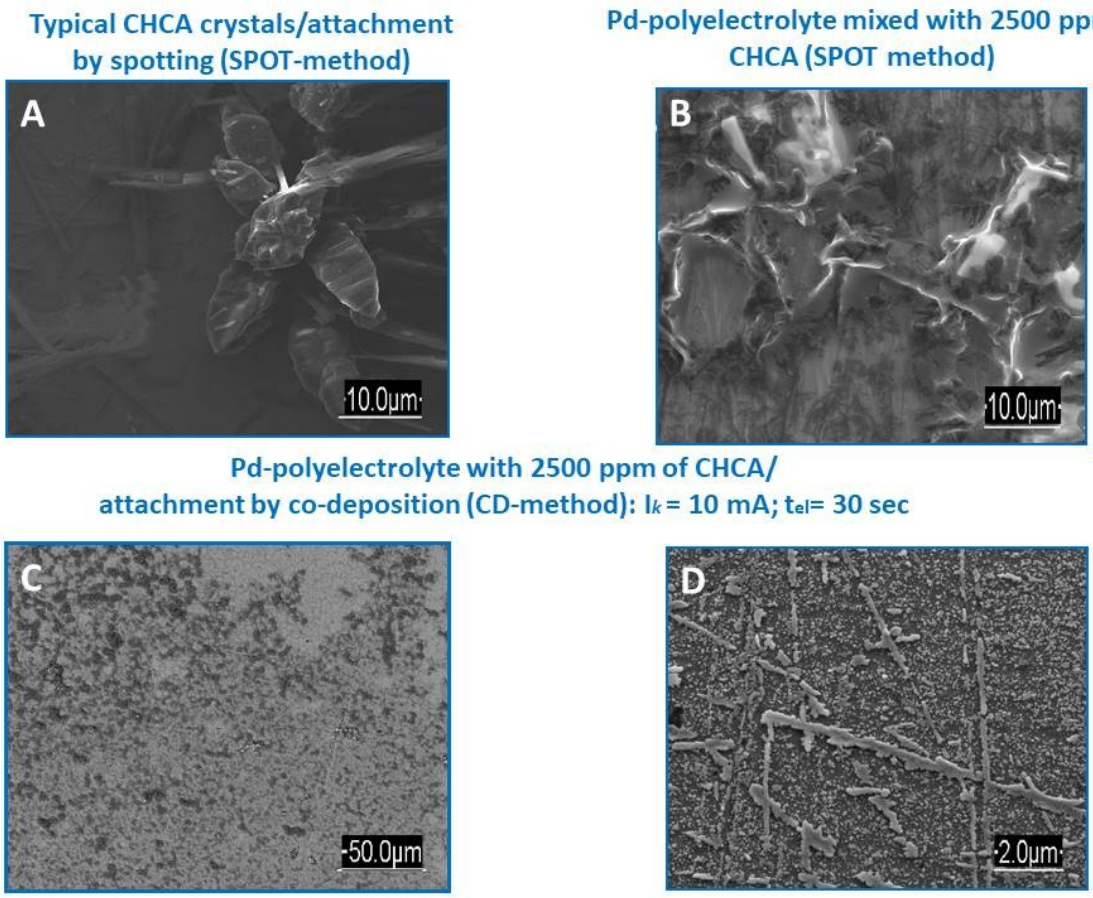


Figure S4. SEM images illustrating evolution of CHCA matrix from macro-stage in SPOT-method to nano-stage in CD-method: (**A**) – pure/spotted CHCA matrix onto the polished steel plate; (**B**) – spotted mixture of CHCA and Pd-electrolyte onto the steel plate; (**C**) – hybrid MALDI/LDI target (Pd-NPs with encapsulated CHCA produced by electroplating; CD-method); (**D**) – the same template as it shown in (**C**) at different magnification.

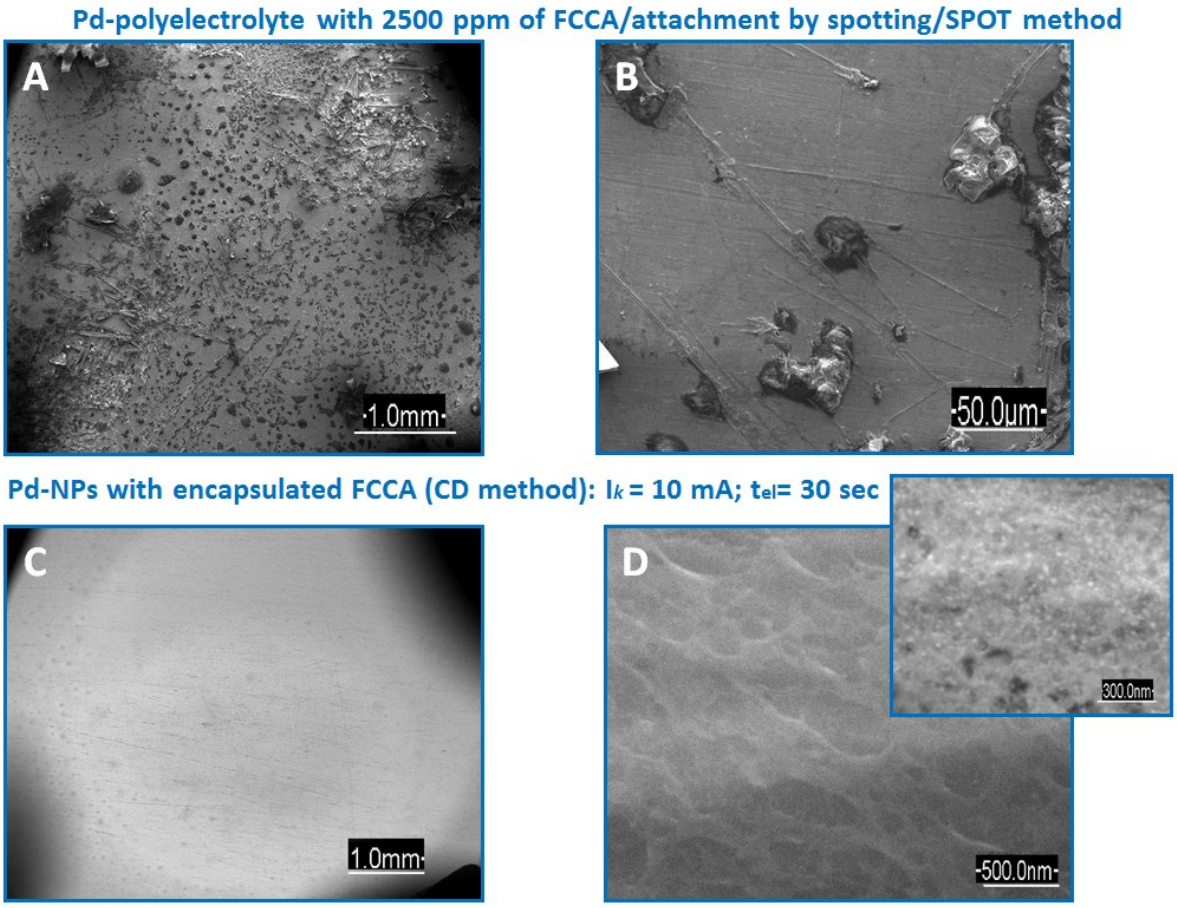


Figure S5. SEM images of the FCCA spotted with Pd-electrolyte and dried at the ambient conditions (**A, B**) and FCCA after encapsulation with Pd-NPs, washed and dried (**C, D**) at different magnification (hybrid MALDI/LDI target).