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Triboelectric nanogenerators for sensitive nano-coulomb molecular mass spectrometry

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ARTICLES

On-Demand Ambient Ionization of Picoliter Samples Using Charge Pulses**

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Scheme 1. Relay electrospray ionization: charge is supplied into (open configuration) or onto the outside (closed configuration) of the sample capillary as ions or charged droplets from a primary source (needle discharge plasma, piezoelectric discharge plasma, or electrospray ion source). The relay generates ions from the analyte solution for mass spectrometric analysis.



- 1. Charge deposition onto or into an ESI emitter, causes an immediate electrospray to occur called relay ElectroSpray Ionization(rESI) technique.
- 2. The positive and negative ion currents of 10–20 nA.
- 3. Analytes were successfully ionized in both the open and closed configurations.

Triboelectric Nanogenerators



a) the contact separation (CS) and b) sliding freestanding (SF) TENGs

- 1. Convert mechanical motion into electricity.
- 2. Charge generation is proportional to surface area, typically in the tens to hundreds of μ C m⁻² per cycle
- 3. Stability upto 10 million cycle.
- 4. Quantized charge generation in the nC range



Measurement of the open-circuit voltage (VOC) and short circuit change transfer (QSC) in TENGs directly using the voltmeter, i.e. the traditional method used studies.1 (a) The in previous equivalent measurement circuit for open-circuit voltage. CV is the capacitance of the voltmeter. (b) The measured QSC for the CS-TENG is 119 nC. (c) and (d) The measured VOC of CS-TENG in the separation-tocontact-to-separation actuations. contact or respectively. (e) The measured QSC for the SF-TENG is 137 nC and (f) open-circuit voltage of the SF-TENG.

- 1. With a CS-TENG, all charges are generated simultaneously at the transient moment when the two triboelectric layers separate.
- 2. SF-TENGs generate charges progressively as the two surfaces slide. With pulse frequency controlled by rate of sliding.
- 3. With SF-TENGs generation of alternating-polarity spray pulses is possible.
- 4. Higher electrostatic voltage can be achieved with SF-TENGs.

Schematic



- 1. controllable ion generation with nC accuracy offered unprecedented control over ion generation.
- 2. The high voltage (5–9 kV) of TENGs provided nanoESI with enhanced sensitivity at low concentrations, while the small number of charges in each ion pulse maximized sample utilization

Electrospray Control



A) Scheme representing how a TENG charges an ion source. B) Time–charge plots describing the ionization pulses from one CS-TENG-driven nanoESI emitter. The four traces are the results of using different resistances: 0 (black), 0.5 (blue), 1 (red) and 1.25 (green) G Ω , in series to regulate the delivered charge

 Q_{pulse} can be controlled by changing R1.

Detection



- the SF-TENG (V_{OC}, 5–9 kV) nanoESI produced a detectable signal at the same concentration level, using the same nanoESI emitter whereas for CS-TENG (VOC, 1.6 kV) and convention d.c. nanoESI (1-2kV) no fragment ion signal was observed. This sensitivity enhancement is believed to be a result of the higher (5–9 kV)
- 2. 13.7nl of 10pgml⁻¹ cocaine ->748spray ->18 pl per spray pulse (~360 molecule)

Application



g) An array of Alexa Fluor 488 fluorescent squares was deposited on an insulating glass cover slide, using a transmission electron microscopy grid as the mask. **h**, On an insulating polyimide tape, the deposited patterned crystal violet spots (\sim 300 µm) were larger than the mask aperture (\sim 200 µm) as a result of the defocusing effect. The other smaller visible features are air bubbles and dust particles trapped in the adhesive layer of the tape. **i**, On a conductive grounded indium tin oxide slide, obtained spots were smaller than the aperture.

Conclusion

- 1. Ion generation by discrete amount of charges enabled by the high output voltage of a TENG.
- 2. Unprecedented control over the ionization process was enabled by quantized ion pulses of adjustable duration, polarity and frequency
- Destructive corona discharge, an issue in the electrospray of aqueous or other high-surface-tension solutions under high voltage, was never observed in any of the ESI experiments using CS-TENGs and SF-TENGs with short circuit charge transfers (QSC) of ~120 nC and ~140 nC, respectively.