

Electrospray deposition in vacuum

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Abstract

We have used the established technique of electrospray in developing a portable vacuum electrospray system which can deposit, in vacuo, dissolved molecules onto a sample which may then be analysed by UHV techniques. As an initial test of the system we have analysed silicon samples with an electrosprayed layer of poly(ethylene) oxide (PEO) using atomic force microscopy (AFM). The polymer forms different structures depending on the voltage applied to the emitter, and solution composition. The system is part of our ongoing effort to deposit other materials such as nanoparticles, and large dye molecules for developing molecular dye sensitised solar cells.

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1. Introduction

Our group has an established research program studying the physics of dye sensitised solar cells [1], including synchrotron radiation investigations of the geometry and charge transfer of constituents of dye molecules such as isonicotinic acid and bisonicotinic acid [2–6], and of small dye molecules [7] on model surfaces. Also of interest are designer molecules which self-assemble on surfaces to form novel nanostructures [8–10]. A limiting factor is the deposition of large, fragile molecules which do not survive sublimation in vacuum. In particular the deposition of species such as N3 dye [11] on clean TiO₂ would give insight into the charge transfer dynamics of molecular solar cells [1]. To address this problem of deposition in vacuum of large molecules, we have used elements of the established electrospray technique, but in vacuum, to deposit molecules onto clean samples which can be analysed by UHV techniques, such as photoemission spectroscopy (PES) or scanning tunnelling microscopy (STM), without exposure to air. This is of vital importance for sample integrity and cleanliness.

Electrospray is widely used in mass spectrometry [12–15] to create gas phase ions of large molecules such as large polymers and proteins. Electrospray essentially involves a solution of the

molecule of interest passing along a capillary to an emitter held at a high voltage (typically a few kilovolts). At the emitter tip, the surface tension of the liquid cannot hold the charge which builds up, and the liquid forms a Taylor cone shape [16]. At the tip a cone-jet forms [17] and the liquid undergoes a Coulombic explosion [18] to create an electrospray of charged droplets. These droplets continue to break up, and the solvent evaporates to leave a gas of the molecular ions. The electrospray process usually takes place in air then the spray travels to a lower pressure chamber for analysis. The various stages of electrospray are complicated and are currently being researched. Aside from mass spectrometry, electrosprayed polymers are used to create surface coatings, functional films [19,20], biological arrays [21,22] and electrode coatings [23]. Previously all electrospray work had been performed in air. Ku and Kim [24,25] have studied the electrospray of glycerol in vacuum, but the high viscosity of glycerol makes the physics quite different than for solutions with lower viscosities, such as water, methanol, and toluene, which are good solvents for the materials we wish to spray in vacuum.

Our vacuum electrospray system is designed for portability. The system is modular with chambers of inner diameter ~60 mm which are easily transported. Potential applications of the working vacuum electrospray system are vast: aside from depositing large molecules for self assembly studies, or dye molecules for solar cells investigations, the system can electrospray nanoparticles in order to investigate surface

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topologies [26], and deposit polymers to form new structures [27,28]. In fact, any material may be deposited provided the system is optimised for the molecule and solvents required.

2. Instrumentation

Fig. 1 shows a schematic of the vacuum electrospray system. A 3 m PEEK tube (0.005 in. ID, 1/16 in. OD, Supelco) connects a reservoir of solution to a 20 cm stainless steel capillary (0.005 in. ID, 1/16 in. OD) through a custom-made vacuum flange into Stage 1. The PEEK tubing has a 2 μm filter on the air side to prevent dust blockages. The solution is a 25:75 or 50:50 water/methanol mixture with the molecule to be sprayed dissolved. Stage 1 is at 1×10^{-2} Torr during spray, and $<1 \times 10^{-3}$ Torr without spray maintained by a 70 l s^{-1} turbomolecular pump. An electrospray needle (tip) is mounted on the capillary end using a microtight PEEK fitting (Upchurch Scientific). The custom-made flange has an electrical feedthrough for a high voltage connection to the tip (2.5 kV for a stainless steel tip) which is insulated using nylon tubing to reduce electrical interference. The capillary and tip are mounted on a three-way manipulator for accurate positioning. The reservoir may be pressurised with nitrogen to push the liquid through the tubing. Both fused silica and nanobore stainless steel tips (Proxeon Biosystems) [29] are used, but stainless steel ones are favoured as the smaller inner diameter ($\sim 20 \mu\text{m}$) allows a lower pressure during spray. A continuous flow rate of $\sim 100 \text{ nl min}^{-1}$ can be sustained for several hours.

The sample is mounted on a linear drive to change the tip–sample distance accurately. The sample (or other ion target) is attached via an electrical feedthrough to a picoammeter to monitor the spray current. A LabVIEW program developed in-house is used to plot, in real time, the current from ions hitting a target, which may be the extraction lenses or quadrupole rods as well as the sample. This real time current plot allows the optimisation of the potentials applied to the tip and lenses to give a reliable spray.

Stage 2 has a 70 l s^{-1} turbomolecular pump and a 9000 amu mass quadrupole (ABB Extrel), and is separated from Stage 1 with custom-made electrostatic lenses with a 3 mm diameter orifice for focussing the ion beam. During electrospray, Stage 2 is at $<4 \times 10^{-6}$ due to differential pumping; this pumping scheme allows the electrospray system to be attached to a UHV chamber such as a synchrotron end station. A pressure of $<1 \times 10^{-9}$ is maintained in Stage 3 during spray.

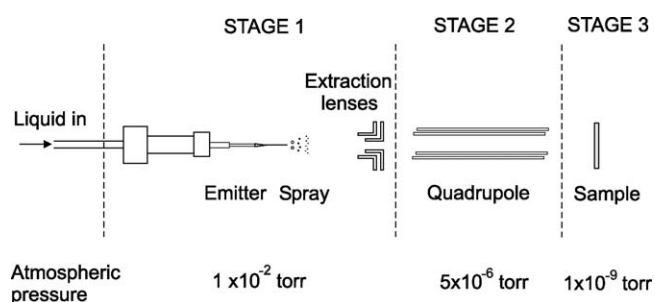


Fig. 1. Schematic of the vacuum electrospray deposition system.

Table 1
Summary of PEO samples

Sample	Emitter voltage (kV)	Time (min)	Concentration (μM)	Sample distance from tip (cm)
I	2.5	15	2.4	4
II	2.5	15	2.4	7
III	4	15	2.4	4
IV	2.5	5	25	4

This table summarises the different conditions used to make the PEO on silicon samples. Sample I is an example of optimal spray conditions; Sample II has a larger tip–sample separation; Sample III uses a high emitter potential; Sample IV uses a high concentration solution.

3. Testing and results

Initial tests were performed to ensure the molecule of interest was passing through the electrospray emitter and adsorbing onto a sample positioned in front of the lenses. Solutions of poly(ethylene) oxide (PEO) in methanol/water mixes were sprayed in vacuum onto silicon substrates (prepared by ultrasonic cleaning in propan-1-ol) as a marker molecule to indicate the performance of the instrument. Details of the solutions and spray conditions used to make different samples are summarised in Table 1. Two PEO samples were prepared in air for comparison to vacuum prepared samples (Fig. 2). A drop-deposited sample was prepared by pipetting a drop of 2.4 μM PEO solution onto a clean silicon sample, and AFM images revealed amorphous blobs of polymer, quite different to the electrosprayed samples.

3.1. PEO sprayed in air

On air-prepared samples, only beads of polymer are present. The emitter was held at 2 kV and the samples have polymer beads $\sim 20 \mu\text{m}$ in diameter imaged with an optical microscope, as shown in Fig. 2a and b. One sample was lightly scratched and studied again, and the area showed dragged polymer-like marks, indicating that the beads observed were indeed PEO and not solution or contaminants. Also of interest is the size of beads in the 2 h and 15 min depositions in air. The increased size of beads in the 2 h sample, as opposed to the increased uniform coverage of the sample, indicate the polymer aggregates into beads after reaching the surface. Also, some of the larger beads in Fig. 2a have begun to merge together. We believe the droplets have formed during a de-wetting process on the surface.

3.2. PEO sprayed in vacuum

A variety of structures were formed by PEO electrosprayed under vacuum. The only structures formed in vacuum which could be observed with the optical microscope ($100\times$ magnification) were long extruded polymer fibres (Fig. 1d) on Sample IV. We attribute the fibre formation to a high solution concentration of PEO. These long fibres may form in the emitter and capillary from the solution evaporating in the vacuum chamber faster than it can be

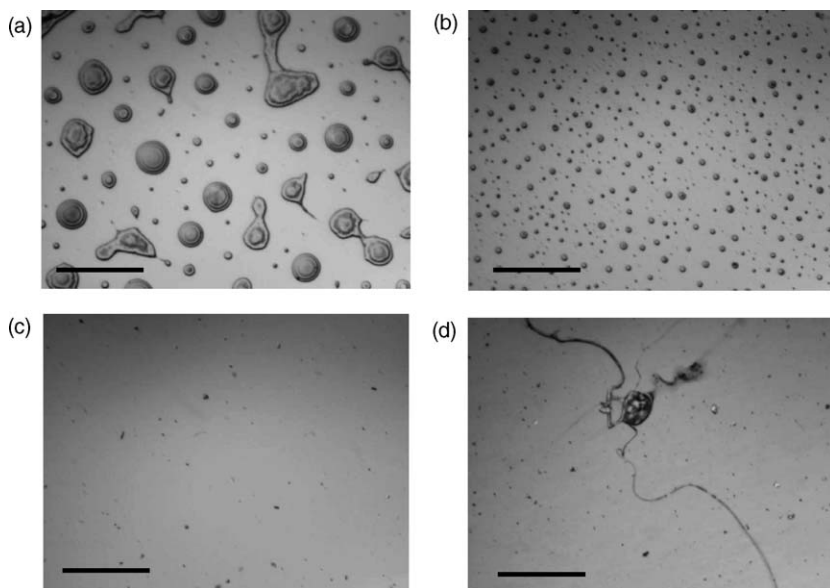


Fig. 2. Optical microscope images taken under 100 \times magnification. (a) Sample prepared in air for 2 h with 2.4 μ M solution; (b) prepared in air for 15 min with 2.4 μ M solution; (c) prepared in vacuum with 2.4 μ M solution for 15 min; (d) prepared in vacuum with 25 μ M solution for 15 min; extruded polymer is visible. Scale bars 50 μ m.

electrosprayed. This explanation is also supported by examining the plot of current with time for the ions reaching the sample. The current measured was erratic, with some periods of no detectable ion current. This could indicate the emitter becomes temporarily blocked with polymer when the fibres form.

All other polymer structures formed on a sub-micron scale and were imaged using an AFM in tapping mode. Beads, strings, and dendrite-like structures were observed, and are shown in Figs. 3–5, respectively. The conditions under which the samples were prepared are summarised in Table 1.

Polymer beads are shown in Fig. 3, and were observed on all samples to some degree. The effects of an increased emitter voltage are shown in Fig. 4a and b, where polymer strings are observed. This qualitative morphology change (beads to strings), with increasing emitter voltage, has also been observed by Morota et al. [30]. This provides evidence that the vacuum electro spray process has characteristics similar to the electro spray process in air. The strings in Fig. 4b

appear to be composed of many beads which are joined together. Other string structures observed from vacuum electro spray include those shown in Fig. 4c–f. These have not been reported in other comprehensive studies of electro sprayed PEO in air [19–22,30]. Further studies are required to ascertain the relationships between air and vacuum electro spray deposition.

Other interesting structures observed are dendrite-like and shown in Fig. 5. Fig. 5b and c are high-resolution areas of Fig. 5a, showing the different patterns produced from spraying a concentrated solution in vacuum (25 μ M). Fig. 5d shows an isolated dendritic feature formed using a high emitter voltage.

4. Discussion and further work

A series of investigations of spraying PEO solutions and also blank solution (water and methanol only) have revealed a number of factors governing successful sample preparation.

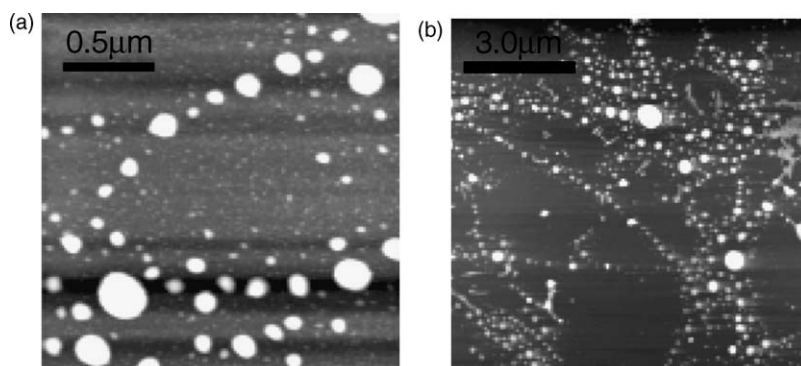


Fig. 3. Bead formations of vacuum electro sprayed samples. (a) Disperse beads from Sample I; (b) beads sometimes line up on the surface, and bare patches lie next to covered areas with obvious boundaries (from Sample IV).

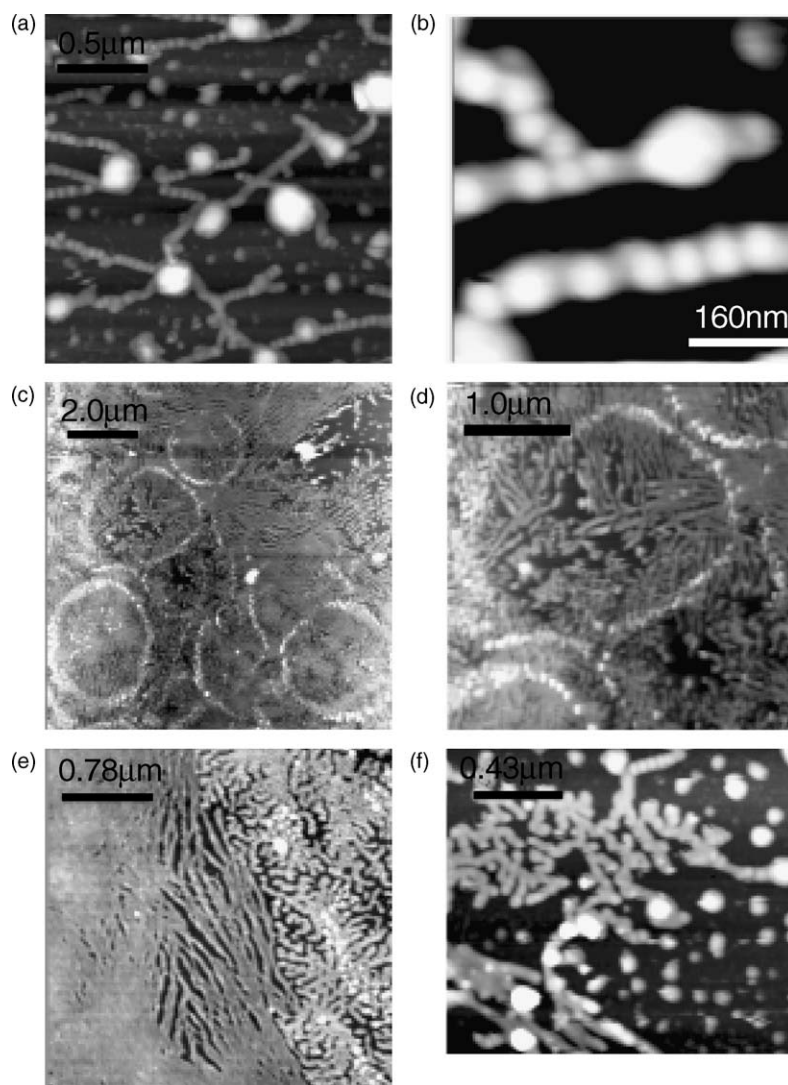


Fig. 4. Varied morphologies of polymer strings: (a) open strings with beads (Sample III); (b) PEO row formed from joined up beads; (c) strings radiating from points give star-like structures (Sample II) with circles on top; (d) close up on (c) showing the star-like formations and the circular marks on top; (e) total coverage on the left, with linear rows and closely spaced irregular rows to the right (Sample III); (f) close up on irregular rows made from beads as in (b) (Sample III).

For a maximum ion current to be measured, the tip–sample separation should be kept to a minimum but still allowing complete desolvation to occur. A more concentrated solution would suggest the sample preparation time can be shorter for a required coverage, as suggested by Sample IV. However, if the solution is too concentrated then the tip can become blocked with accumulated molecule where large polymer extrusions were observed (Fig. 2d). A higher voltage applied to the tip also gives a higher current and different sample morphology (Fig. 4a and 4b) but it is more difficult to achieve a steady current/spray away from the optimal voltage of about 2.5 kV.

Electrospray ionization of salt solutions is problematic. This problem is compounded in vacuum electrospray due to accumulation of the crystallised salt within the emitter. This can be removed by sonic cleaning of the emitter which is only possible with stainless steel tips. We are currently investigating this using very low concentrations of salts in electrospray solution.

In order to spray dye molecules onto TiO_2 surfaces with a view to studying charge transfer dynamics of model molecular solar cells, the vacuum electrospray system can be attached to a UHV system for sample analysis, for example a synchrotron beamline or a photoemission spectrometer. While there are many aqueous nanoparticles suspensions which can be used for electrospray deposition, it is worth noting that many important nanoparticles and clusters are soluble only in organic solvents, such as toluene. Vacuum electrospray using organic solvents is currently a challenge due to these solvents freezing at the emitter tip because of the low pressure and their high volatility. Methods of heating the tip to overcome these effects are currently being investigated. In principle, the range of molecules which may be deposited using vacuum electrospray deposition is limited only by the availability of suitable solvents. The only restriction placed on the choice of sample substrate is that it should be conducting to some degree in order to prevent charging under the flux of ions.

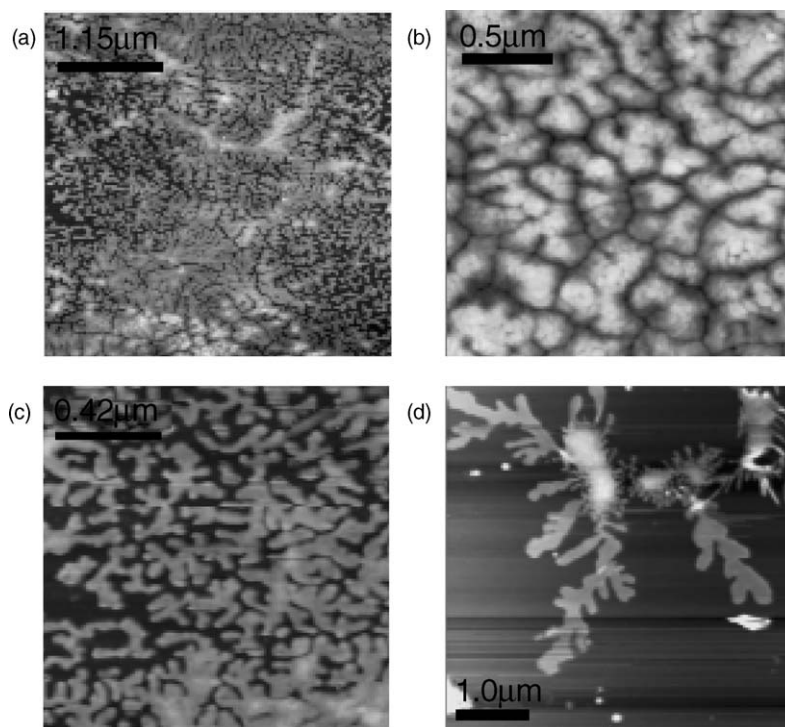


Fig. 5. Dendrite-like structures. (a) Large area image showing rough covered areas (bottom) next to curvy dendritic structures and bare silicon (Sample IV); (b) close up on rough coverage; (c) close up on curvy dendritic structures; (d) isolated dendrite, of different appearance to those in (c) (Sample III).

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