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Supporting Information

Obtaining Thickness-Limited Electrospray Deposition for 3D Coating

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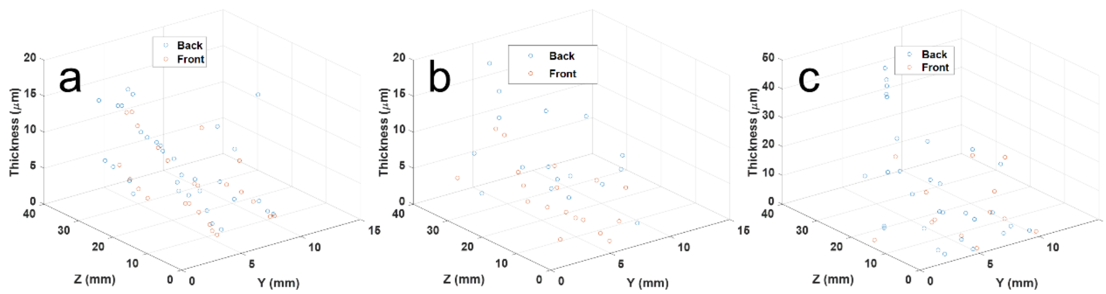

Figure S1. 3D scatter plots of coating thicknesses measured on knight statues shown in Figure 5. (a) corresponds to Figure 5a,d, (b) corresponds to Figure 5b,e, and (c) corresponds to Figure 5c,f.

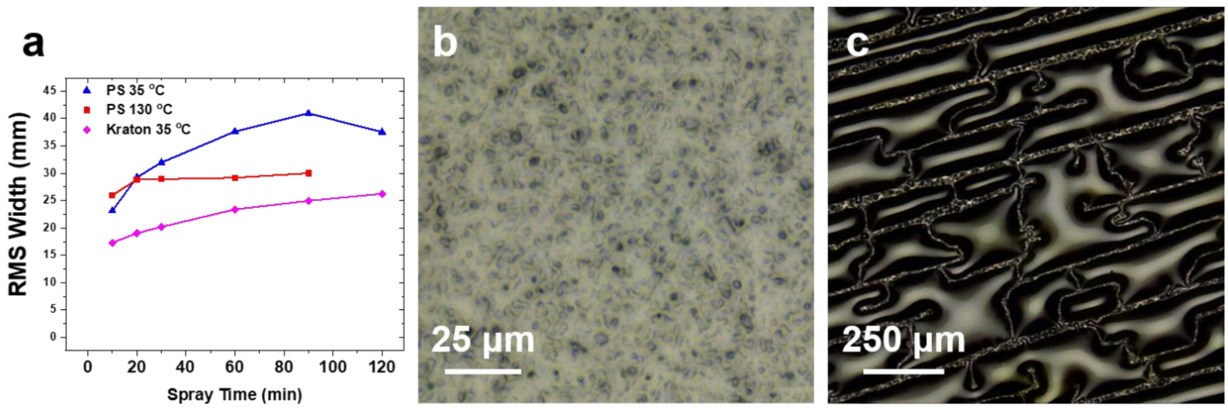

Figure S2. Indicators of charged melt spray. (a) The RMS width of profiles from characteristic sprays as a function of time. It should be noted that the spot is often asymmetric and the narrowest region is selected for measurement; however, it is still apparent that the Kraton profile has a lesser extent to other sprays. This also indicates that the actual spray spot, which is likely a similar size to the Kraton profile does not directly correlate to the size of SLS spray. (b,c) Other morphologies of TB cells. (b) Optical image of TB cells from Kraton sprayed at 35 °C for 120 min at a flow rate of 0.5 mL/h from a 1 wt % 2-butanone solution displaying smaller cellular morphologies. (c) Optical image of TB cells from PS sprayed at 150 °C for 60 min at a flow rate of 0.5 mL/h from a 1 wt % 2-butanone solution, forming islands rather than holes.

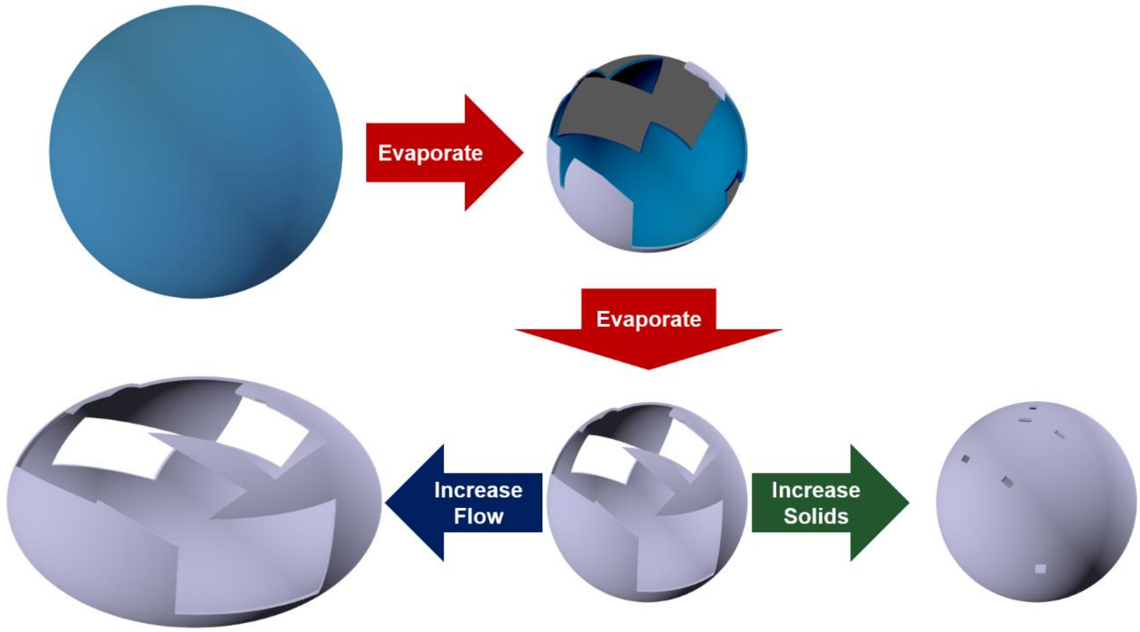

Figure S3. Schematic of polystyrene particle formation. Particles precipitate on the surface of the evaporating droplet to form a shell. Droplets with larger solids loadings form more complete shells, while droplets sprayed at a higher flow rate lead to larger particles.

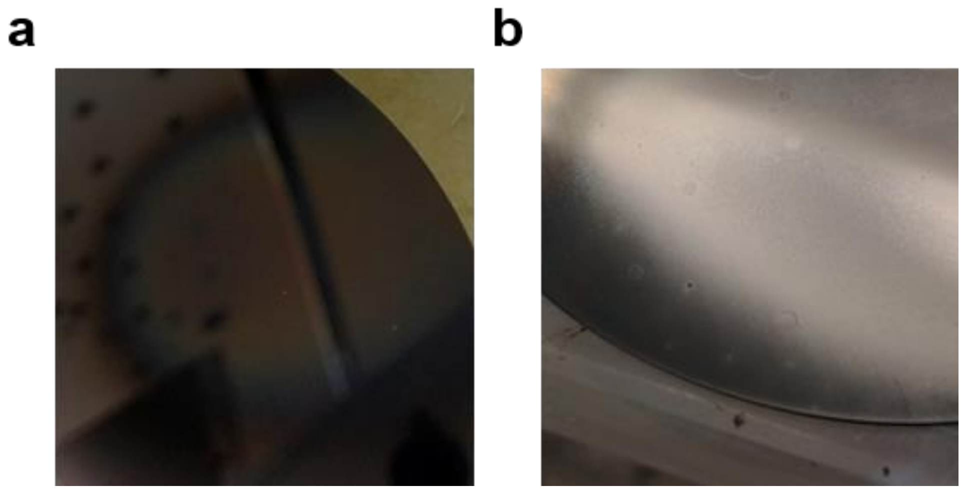

Figure S4. (a) Photograph taken during a spray of 0.1 wt % poly(acrylic acid) in isopropyl alcohol conducted at a 6 cm spray distance at room temperature with a flow rate of 0.5 mL/h to repeat conditions reported in Altmann et al.[1] The smoothness of the film, evidenced by the reflectance coloration, is indicative of electrowetting spray at an optical thickness. (b) Photograph after 5 hours of spray, displaying thickness-limited behavior. The peak thickness was measured to be 1.18 μm.

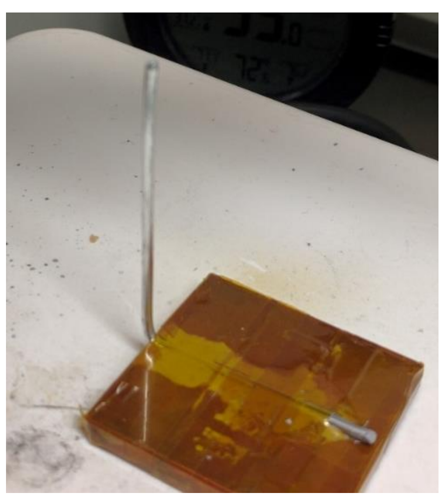

Figure S5. Photograph of uncovered stripe of material on a stainless steel wire typical of electrowetting or charged melt coverage of a 3D object.

Droplet Size Extrapolation

Properties relevant to electrospray of 2-butanone and acetone are listed in Table S1 from the Shell datasheets for each solvent.

Table S1. 2-butanone and acetone properties

Solvent	Boiling Point (°C)	Surface tension (mN/m)	Density (kg/m^3)	Electrical Conductivity (S/m)
2-butanone	80	25	805	$2x10^{-5}$
acetone	56	24	791	$2x10^{-5}$

Based on these properties and data from Gañán-Calvo et al[2] we were able to extrapolate to the range of our experiments using Eq. 1 with values of $\alpha = 2.36$ and $d_0 = 2.47$ µm. The fitting, which had R^2=0.98, is shown in Figure S6.

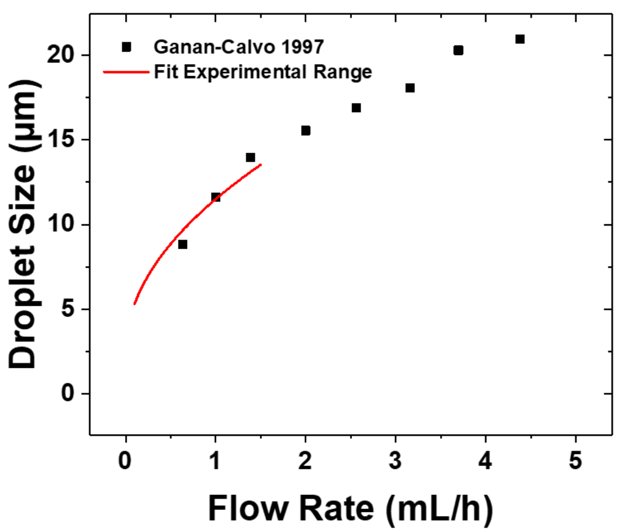

Figure S6. Experimental data for acetone along with fit from Eq. 1 for the relevant experimental range of the reported experiments.

Simulation Details

Electrostatic simulations were conducted using COMSOL multiphysics. The cell was modeled as a radius and height 10 cm axisymmetric geometry with 0 charge on the top and side surfaces and a grounded base. The spray needle was simulated as a 0.1 cm radius and 6 cm height with 5 kV of charge to make a 4 cm needle to surface difference. The polymer coating was simulated as a cylindrical dielectric coating of 500 µm thickness and 50 $\mu C/m^2$ surface charge with different cylinder radius.

Experimental Parameters

The table below lists all experimental parameters used in experiments. Lab room temperature is not controlled to a high precision and could fluctuate between 15~25 °C during a given experiment. Ambient humidity was also not controlled and could vary from 20~60%. For a majority of experiments, initial humidity was recorded, but could vary during the experiment. Statue demonstrations were done before humidity monitoring was available and also often required frequent minor alterations in the external field during the experiment to maintain stability.

Table S2. Experimental Parameters for Electrospray

Sample Series	Spray Distance (cm)	Spray Time (min)	Flow Rate (mL/h)	Needle/Ring Voltage (kV)	Initial Ambient Humidity (%)	Solids Concentration (wt %)	Polymer	Spray Temperature (°C)
Kraton time	4.0	10	0.50	5.6/2.8	24.6	1.0	Kraton	35
		20			26.1			
		30			26.1			
		90			29.6			
		120			31.6			
Polystyrene time	4.0	10	0.50	5.4/2.8	30.0	1.0	Polystyrene	35
		20			30.0			
		30			30.0			
		60			30.0			
		90			30.0			
		120			20.2			

	4.0	10			22.1	1.0	Polystyrene	70
		20			22.1			
		30			23.8			
		60			23.3			
		90			24.5			
	4.0	10			23.6	1.0	Polystyrene	100
		20			23.6			
		30			22.3			
		60			22.9			
		90			21.4			
	4.0	10			31.3	1.0	Polystyrene	130
		20			36.6			
		30			33.4			
		60			33.4			
		90			33.7			
Polystyrene temperature	4.0	60	0.50	5.5±0.2/2.8	19.3	1.0	Polystyrene	35
					19.3			70
					26.2			85
					22.9			100
					20.9			130
					28.7			150
Polystyrene flow rate	4.0	300	0.10	5.2±0.3/2.7±0.2	24.0, 18.3, 27.2	1.0	Polystyrene	35
		120	0.25		40.8,19.3			
		60	0.50		40.2,19.0			
		30	1.00		44.3,19.1			
		20	1.50		44.3,19.1			
	4.0	300	0.10	5.4±0.2/2.8	46.9, 24.8, 27.1	1.0	Polystyrene	70
		120	0.25		30.6, 23.2, 43.6			
		60	0.50		27.1, 23.2, 27.2, 27.2, 27.2, 23.3, 23.3			
		30	1.00		30.6, 23.7			
		20	1.50		24.2, 17.7			
	4.0	596.2	0.50	5.5/2.8	23.6, 44.9	0.1	Polystyrene	35

Polystyrene solids loading		119.2			26.2, 35	0.5		
		59.6			26.2, 38.9	1.0		
		29.8			26.2, 37.4	2.0		
		14.9			24.7, 32.4	4.0		
	4.0	596.2	0.50	5.5/2.8	20.5, 35.5	0.1	Polystyrene	70
		119.2			26.4, 36.0, 18.2	0.5		
		59.6			24.9, 37.9	1.0		
		29.8			24.9, 36.5	2.0		
		14.9			26.4, 35.1	4.0		
Polystyrene field	4.0	30	0.5	5.2/2.4	19.4	1.0	Polystyrene	35
				6.0/3.7	19.8			
				7.0/5.1	19.0			
	4.5			5.2/2.2	26.5			
				6.0/3.5	26.7			
				7.0/3.5	25.8			
	5.0			5.2/2.2	18.8			
				6.0/3.5	18.8			
				7.0/4.9	19.8			
Melting gel time	4.0	10	0.63	5.4±0.1/2.5	44.0	1.0	MG 65/35	RT
		20			44.3			
		30			44.6			
		60			41.4			
		90			43.3			
		150			20.0			
	4.0	10	0.63	5.4/2.5	32.4, 17.6, 20.5, 34.2	1.0	MG 87/13	RT
		20			32.3, 17.6, 20.5, 31.2			
		30			32.0, 19.0, 20.5, 31.2			
		60			31.3, 19.0, 20.7, 28.8, 19.6, 21.3			
		90			20.2, 20.4, 27.3			
		150			32.0			
Melting gel temperature	4.0	60	0.50	5.4/2.8	28.2	1.0	MG 65/35	RT
					28.2			75

					28.2			145
					28.2			175
					28.2			205
Stainless steel wire	5.0 (wire top)	60	0.50	6.7/--	26.7	1.0	Polystyrene	RT
	5.0 (wire top)		0.50	6.7/--	24.1		Polystyrene	120
	6.7 (wire top)		0.63	7.2/--	23.2		MG 87/13	RT
3D pewter statues	8 (statue top)	180	0.55	~6/--	20~60	1.0	Polystyrene	RT
	6 (statue top)	180	0.50	~7/--	20~60		Polystyrene	
	3 (statue top)	180	0.63	~9/--	20~60		MG 87/13	
Polystyrene mass time	4.0	6.6	1.50	5.6/2.7	18.2	1.0	Polystyrene	35
		10			18.2			
		20			18.2			
		30			18.3			
	4.0	30	0.50	5.4/2.8	31.2	0.5	Polystyrene	35
		60			31.2			
		120			26.2			
		180			33.2			

References

(1) Altmann, K.; Schulze, R. D.; Hidde, G.; Friedrich, J. Electrospray ionization for deposition of ultra-thin polymer layers – principle, electrophoretic effect and applications. *Journal of Adhesion Science and Technology* **2013,** *27* (9), 988-1005.

(2) Gañán-Calvo, A. M.; Dávila, J.; Barrero, A. Current and droplet size in the electrospraying of liquids. Scaling laws. *Journal of Aerosol Science* **1997,** *28* (2), 249-275.