Deposition of PPy-C8F onto PS seed particles

The following protocol was used for coating the 20 μm-sized polystyrene (PS20) particles with a polypyrrole (PPy-C8F) overlayer. Pyrrole (0.48 g, 4.0%) was added by syringe to a PS aqueous dispersion (144 g water and 12 g PS particles) in a 500 mL screw-capped bottle and the system was left for 3 h with magnetic stirring. C8F aqueous solution (40 wt%, 2.98 g) was then added to the dispersion. FeCl3·6H2O oxidant (4.51 g) was dissolved in 96 g water and added to the aqueous dispersion of PS particles. The polymerisation was allowed to proceed for 24 h at 500 rpm using a magnetic stirrer. PPy-C8F coating of the other PS seed particles with diameters of 40, 80 and 140 μm were also conducted by the chemical oxidative aqueous seeded polymerisation in the same manner, though the ratio of pyrrole monomer and the total surface area of the seed particles was adjusted to be the same as that of the 20 μm PS particle system see Table S1. The PPy-C8F-coated PS particles were subsequently purified by repeated centrifugation-redispersion with sonication cycles (successive supernatants were replaced with de-ionised water) in order to remove the unwanted by-products (PPy-C8F homopolymer, FeCl2 and HCl), followed by freeze-drying overnight. PPy-C8F bulk powder was synthesised by chemical oxidative precipitation polymerization as described in our previous study. The nitrogen composition obtained by elemental analysis is also given in Table S1.

Table S1. Synthetic and particle characterisation data

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Pyrrole monomer concentration (wt%)</th>
<th>Nitrogen composition from elemental microanalysis (%)</th>
<th>Experimental PPy-C8F loading, x (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS20/PPy-C8F</td>
<td>4.0</td>
<td>0.32</td>
<td>5.0</td>
</tr>
<tr>
<td>PS40/PPy-C8F</td>
<td>2.0</td>
<td>0.07</td>
<td>1.1</td>
</tr>
<tr>
<td>PS80/PPy-C8F</td>
<td>1.0</td>
<td>0.05</td>
<td>0.8</td>
</tr>
<tr>
<td>PS140/PPy-C8F</td>
<td>0.6</td>
<td>0.05</td>
<td>0.8</td>
</tr>
<tr>
<td>PPy-C8F</td>
<td>-</td>
<td>6.41</td>
<td>100</td>
</tr>
</tbody>
</table>

Polypyrrole shell layer thickness calculation

The shell layer thickness on each core-shell particle sample was calculated according to Eq. S1 below for which \( r_1 \) is the PS core radius (μm), \( r_2 \) is the PS/PPyC8F core-shell radius (μm) as depicted in Fig. S1. \( x \) is the mass % of PPy-C8F in the particle calculated by comparison to pure PPy-C8F homopolymer in Table S1.

\[
r_2 = \frac{3}{\sqrt{5}} \left( \frac{r_1^3}{1 + \frac{x}{100 - x} \times \frac{PS \text{ density}}{PPy-C8F \text{ density}}} \right) = \frac{3}{\sqrt{5}} \left( r_1 \mu m \right)^3 \times \left( 1 + \frac{x}{100 - x} \times \frac{1.06 \times 10^{-15} \text{ g/μm}^3}{1.85 \times 10^{-12} \text{ g/μm}^3} \right)
\]  

(Eq. S1)
Statistical model

As in Ireland et al. we use a weakest-link failure model, with the particle extraction probability given by a 3-parameter Weibull distribution. This type of model is frequently used to predict failure in brittle solids, where an unknown but statistically quantifiable distribution of precursor flaws is present. We assume that the probability of any specific particle in the area of interest being released from the bed can be given by:

\[ P_j = 1 - \exp \left[ - \left( \frac{f_z - f_u}{f_0} \right)^m \right] \]  

(S2)

\( f_z \) is the electrostatic extracting force in the normal direction per unit area of the top of the bed at the position of the single particle – i.e. the electrostatic pressure. This plays the same role as the tensile stress in fracture models. \( f_u \) is the minimum electrostatic pressure at which a particle will be extracted. \( f_0 \) is a characteristic value giving the scale of the distribution; namely, the value of \( f_z - f_u \) at which the probability of extraction of a randomly-selected particle is \( 1 - e^{-1} \). The index \( m \) affects the spread of electrostatic pressures at which particle extraction occurs, a higher value indicating a narrower spread of pressures. \( f_u, f_0 \) and \( m \) are all characteristics of the bed, independent of the electric field. The effects of particle size, cohesiveness, etc. are all incorporated into these parameters.

The probability that a given particle cannot be extracted is the complement of \( P_j \), i.e.

\[ 1 - P_j = \exp \left[ - \left( \frac{f_z - f_u}{f_0} \right)^m \right] \]  

(S3)

For an area containing \( N \) identical particles, subjected to a uniform electrostatic pressure, the probability that none of them will be extracted is given by

\[ 1 - P^\text{ensemble}_j = (1 - P_j)^N \]  

(S4)

Thus, for an area \( A \) with \( \rho \) particles per square metre (i.e. \( N = \rho A \)), we can rearrange Eq. S2 to obtain the probability that at least one particle will be extracted, \( P_0 \):

\[ P_0 = 1 - \exp \left[ -\rho A \left( \frac{f_z - f_u}{f_0} \right)^m \right] \]  

(S5)

If the electrostatic pressure is non-uniform on the area of interest, Eq. S4 must be integrated over the affected area of the top of the bed. For a radially-symmetric field, as in this case, this is:

\[ P_0 = 1 - \exp \left[ -2\pi \rho \int_0^{r_{\text{max}}} \left( \frac{f_z - f_u}{f_0} \right)^m r \, dr \right] \]  

(S6)

where \( r \) is the radial distance from the axis of the system and \( r_{\text{max}} \) marks the outer edge of the area of interest. The electric field is approximated by that between a conducting plane and sphere, using the model of Morrison (1989). Since the bed is assumed to be conducting, the electric field at its surface is assumed to be entirely normal to the surface. The electrostatic normal pressure will be given in terms of the normal electric field, \( E_z \), by

\[ f_z(r) = \sigma(r)E_z(r) \]  

(S7)
where \( \sigma \) is the charge per unit area of the top of the bed. By Gauss’s Law,

\[
\sigma(r) = \varepsilon_0 E_z(r)
\]

(S8)

where \( \varepsilon_0 \) is the permittivity of free space, and thus

\[
f_z(r) = \varepsilon_0 E_z(r)^2
\]

(S9)

According to the field model,

\[
f_z(r) = \frac{\varepsilon_0 V^2}{a^2} \times H(\alpha, \delta)
\]

(S10)

where \( V \) is the driving voltage, \( a \) is the sphere (drop) radius, \( \alpha = r/a \) is the dimensionless radial coordinate and \( \delta = h/a \) is the dimensionless sphere-plane separation. \( H \) is thus a function that gives the distribution of the electrostatic pressure in terms of the dimensionless geometry of the system. If we let \( H_\mu \) be the minimum extraction pressure, \( f_\mu \), made dimensionless by the same scaling as in Eq. S10, we can now write

\[
P_0 = 1 - \exp \left[ -2\pi \rho a^2 \int_0^{a_{\text{max}}} \frac{[H(\alpha, \delta) - H_\mu]^m}{a} \, da \right]
\]

(S11)

The integral in Eq. S11 cannot be evaluated analytically, and must be determined numerically for \( m, H_\mu \) and \( \delta \). This was done for a set of over 4000 points covering the entire relevant range of these parameters, and invertible interpolation functions found. We denote these functions corporately as

\[
G(\delta, m, H_\mu) \cong \int_0^{a_{\text{max}}} [H(\alpha, \delta) - H_\mu]^m \, da
\]

(S12)

and thus:

\[
G(\delta, m, H_\mu) \cong -\frac{1}{2\pi \rho a^2} \left( \frac{f_\mu a^2}{\varepsilon_0 V^2} \right)^m \ln(1 - P_\mu)
\]

(S13)

allowing us to determine the height at which the first particle is extracted from the bed, \( h_0 \), as a function of the probability, \( P_0 \):

\[
\frac{h_0}{a} = \delta_0 \cong G^{-1}(m, H_\mu) \left[ -\frac{1}{2\pi \rho a^2} \left( \frac{f_\mu a^2}{\varepsilon_0 V^2} \right)^m \ln(1 - P_0) \right]
\]

(S14)

where \( G^{-1}(m, H_\mu) \) indicates inversion with respect to \( \delta \) only (i.e. for given values of \( m \) and \( H_\mu \)). It is now possible to determine the envelope of separations where the first particle is observed to be extracted from the bed for a given driving voltage and probability range (e.g., 5% to 95%) and compare these to drop-bed separation data. It is worth noting that \( \rho \) and \( f_\mu \), if both unknown, are not individually distinguished by the model; we therefore let

\[
K = \frac{2\pi \rho}{f_\mu}
\]

(S15)

and thus

\[
h_0 \cong aG^{-1}(m, H_\mu) \left[ -\frac{1}{K \varepsilon_0 V^2 a^{2m-2}} \ln(1 - P_0) \right]
\]

(S16)

It remains to determine which values of \( m, K \) and \( f_\mu \) are most consistent with a set of voltage-bed separation data. For each experimental data point \( i \), Eq. S6 is used to calculate the significance (i.e. the theoretical probability of occurrence) of the measured drop-bed separation for \( V \), and for proposed values of \( m, K \) and \( f_\mu \). This significance measure is denoted \( S_i \). If the model is correct, a plot of cumulative frequency vs. significance for a large number of data points, \( N \), will be a straight line through the origin with slope \( N \). Thus, a least-squares linear regression analysis is performed between the set of cumulative frequency vs. \( S_i \) data, and this ‘ideal’ cumulative frequency distribution.
Comparison of PS40 and PS80 data for drop-bed separation

![Graph showing drop-bed separation distance as a function of applied potential for PS40 and PS80 particles.](image)

Figure S2. Measured drop-bed separation distance when uncoated particles are first observed to be extracted from the bed, as a function of applied potential. Both PS particle samples are used as received from supplier. At higher potentials, PS40 particles are not observed to be extracted from the bed, due to increased cohesion. All data points shown here sit below those of the samples shown in the main text, due to decreased conductivity and therefore an increased difficulty in extraction.⁶

References