Electrostatic Self-Assembly of Polystyrene Microspheres by Using Chemically Directed Contact Electrification**

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Herein we describe a process—based on contact electrification and electrostatic interactions—that directs the self-assembly of chemically modified polystyrene microspheres to form three-dimensional microstructures. When two solid surfaces are brought into contact and separated, charge is often transferred from one surface to the other in a process known as contact electrification.[1,2] We can predictably and rationally control the contact electrification of polystyrene microspheres, and use the resulting charged materials for electrostatic self-assembly. We control the contact electrification of these microspheres by introducing immobilized ions and mobile counterions: the choice of these ions determines the electrostatic charges that these beads acquire through contact before and during the assembly process. Oppositely charged microspheres assemble into uniform spherical microstructures under the influence of electrostatic forces. Sequential steps of self-assembly can create multilayered microstructures.

There are many examples of electrostatic self-assembly of charged ions, polyelectrolytes, and colloids in solution.[3–8] Xerography, an example of dry electrostatic self-assembly, uses corona discharge from a high-voltage electrode to create a charge on the imaging drum, and contact electrification to create an opposite charge on the toner particles.[9] Contact electrification can also direct the self-assembly of millimeter-sized spheres into ordered two-dimensional lattices.[10] (That process used the inherent differences in contact electrification of various polymers, in contrast to the rational, chemically directed contact electrification we describe herein.) Patterns of charge, created by electron-beam writing,[11] an atomic force microscopy (AFM) tip,[12] or electrical microcontact printing[13] on a dielectric surface, can guide the self-assembly of micro- or nanoparticles with sub-100 nm lateral resolution.[14]

Although contact electrification is a familiar phenomenon, the detailed mechanisms of contact electrification are not known, and it is likely that different mechanisms may be involved depending on the specific materials and environmental conditions. There is one class of materials that exhibits

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predictable contact electrification and for which Diaz and co-workers have proposed a plausible mechanism of charge-transfer:[15–17] the contact charging of ionomers (polymers with covalently bound ionic functional groups) is believed to result from the transfer of mobile ions from the ionomer to another material (Figure 1).
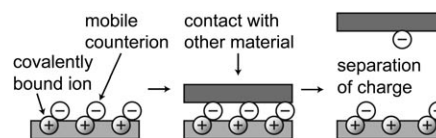

Figure 1. A schematic representation of the ion-transfer model of contact electrification.

According to this model, an ionomer with covalently bound cations transfers some of its mobile counterions to another surface upon contact; this transfer results in a positive charge on the ionomer, and a negative charge on the other surface. Using an ionomer with covalently bound anions would yield the opposite charges. Diaz and co-workers compiled extensive experimental support for this mechanism, including X-ray photoelectron spectroscopy (XPS) measurements of the contacted surface that demonstrate transfer of the mobile ion but not the covalently bound ion.[18] Because this mechanism for the contact electrification of ionomers is reasonably well-understood, it is possible to rationally design components to become charged through contact electrification, and use those components for electrostatic self-assembly.

We prepared poly(styrene-*co*-divinylbenzene) microspheres with covalently bound tetraalkylammonium functional groups (**1**) and covalently bound sulfonate functional groups (**2**) as shown in Scheme 1. The azobenzene moiety in **2** imparted an orange color to those beads, while the other beads (**1**) were colorless. We prepared beads with diameters ranging from 5 to 200 μm with both types of functionality, and characterized the insoluble cross-linked beads by elemental analysis and IR spectroscopy. (The Supporting Information provides experimental details.)

We investigated the contact electrification of each type of bead using the following procedure: About 40, 200-μm-diameter beads were agitated in a 5-cm-diameter aluminum dish for approximately 5 min. We measured the charges on individual beads using a device described in the Supporting Information; briefly, the device consisted of an aluminum tube connected to an electrometer. As individual charged beads were passed through the tube, the electrometer recorded the charge induced on the exterior of the tube.
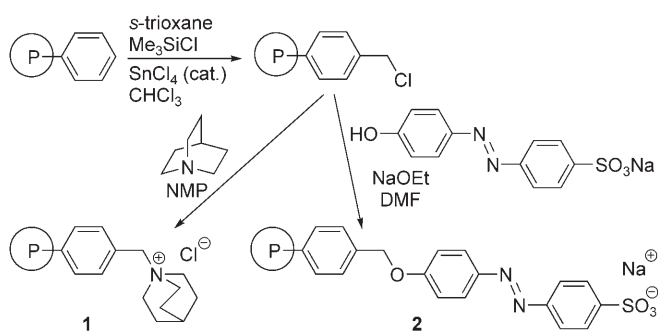
Scheme 1. Chemical modification of cross-linked polystyrene microspheres to yield spheres with tetraalkylammonium (**1**) and sulfonate (**2**) functional groups. The Supporting Information provides experimental details. NMP = 1-methyl-2-pyrrolidone, DMF = dimethylformamide, P = polymer.

According to Gauss's Law, this induced charge is the same as the charge on the bead.

Figure 2 shows histograms of charge measurements of 200-μm beads with each type of functionality. As predicted by the ion-transfer hypothesis, all of the beads with the tetraalkylammonium functionality (**1**) were positively charged, while all of the beads with the sulfonate functionality (**2**) were negatively charged. Assuming that the charge is uniformly distributed on the surface of each bead, the magnitude of the charge (ca. 0.01 nC per bead) corresponds to approximately one elementary charge per 2000 nm². Since the density of ionic functional groups on the surface of each bead is probably on the order of one functional group per 10 nm², only about 0.5% of the mobile ions on the bead surface are transferred during contact electrification.
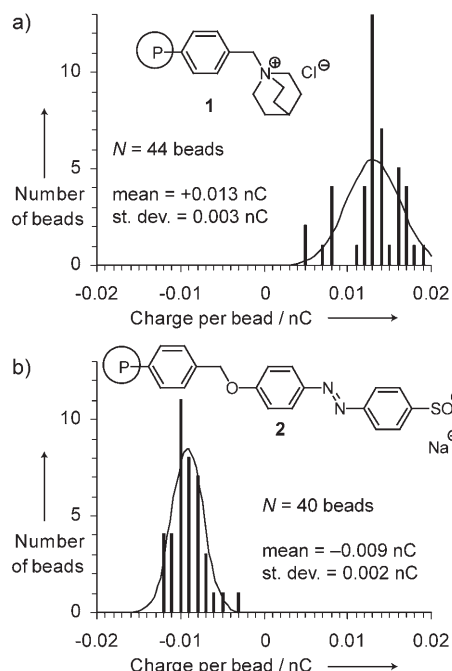

Figure 2. Histograms (with normal distributions superimposed) of the measurements of charges on individual 200-μm-diameter beads. a) Tetraalkylammonium beads (**1**). b) Sulfonate beads (**2**). N = sample size, st. dev. = standard deviation.

Figure 3a shows a schematic representation of the process of self-assembly. In a typical experiment, we combined approximately 0.5 mg of dry, 200-μm-diameter sulfonate-functionalized beads (**2**) with approximately 0.5 mg of dry, 20-μm-diameter tetraalkylammonium-functionalized beads (**1**) in an aluminum dish. We agitated the dish until the beads were thoroughly mixed. Within seconds, each orange 200-μm bead (**2**) became coated with a slightly disordered monolayer of the colorless 20-μm beads (**1**), as shown in Figure 3b. Mixtures with the charges reversed (i.e., the larger sphere was positively charged) or with different sizes of microspheres yielded similar structures. We reproduced these results under a wide range of ambient laboratory conditions (ca. 20–25°C and ca. 30–80% relative humidity (RH)). The smallest assemblies were achieved with a combination of 5-μm and 50-μm beads (shown in the Supporting Information as Figure S1.) When the two oppositely charged spheres were the same size, extended aggregates formed with local Coulombic ordering (e.g., (+)(−)(+)(−)) but no long-range order.

To achieve uniform coverage of the large spheres, we used an excess of the small spheres (at least 10-times more than would be needed for monolayer coverage). Thus, we considered the large spheres in these experiments to be the "limiting reactant." We determined the yield of our experiments by identifying on each large sphere any vacant areas large enough to bind a small sphere; each such defect was considered to be a site of incomplete "reaction" of the small spheres with the large sphere. In the large-field image shown in Figure 3b, there were 100 complete assemblies (including those hidden by the inset), each with about 100 visible small spheres. We found only six vacant sites in the entire image, for a yield of greater than 99.9%.

Each monolayer assembly had an overall net charge, as shown by the response of an assembly to an applied electric field (ca. 1 kV cm⁻¹). The sign of the charge was the same as that of the smaller (outer) beads in the assembly. Coulombic interactions between nonpolarizable charged spheres can explain the stability of these assemblies. As detailed in the Supporting Information, simple electrostatic calculations show that one of these structures can have a net electrostatic charge and still have a negative total electrostatic energy. In this case, the electrostatic attraction between the small spheres and the large central sphere is greater than the electrostatic repulsion between the small spheres, even when the small spheres are close-packed on the surface.

Since the assemblies had a net charge, we attempted to use them as components in subsequent steps of self-assembly. Shaking and tapping, however, disrupted the assemblies. Heating the assemblies to approximately 260°C for 10–15 min annealed the beads together, and made the assemblies more robust mechanically. After annealing, we could use the charged composite structures as components in a subsequent assembly step (Figure 3a) to yield multilayered microstructures (Figure 3c). This process is reminiscent of the layer-by-layer electrostatic self-assembly of polyelectrolytes in solution.[5,8]

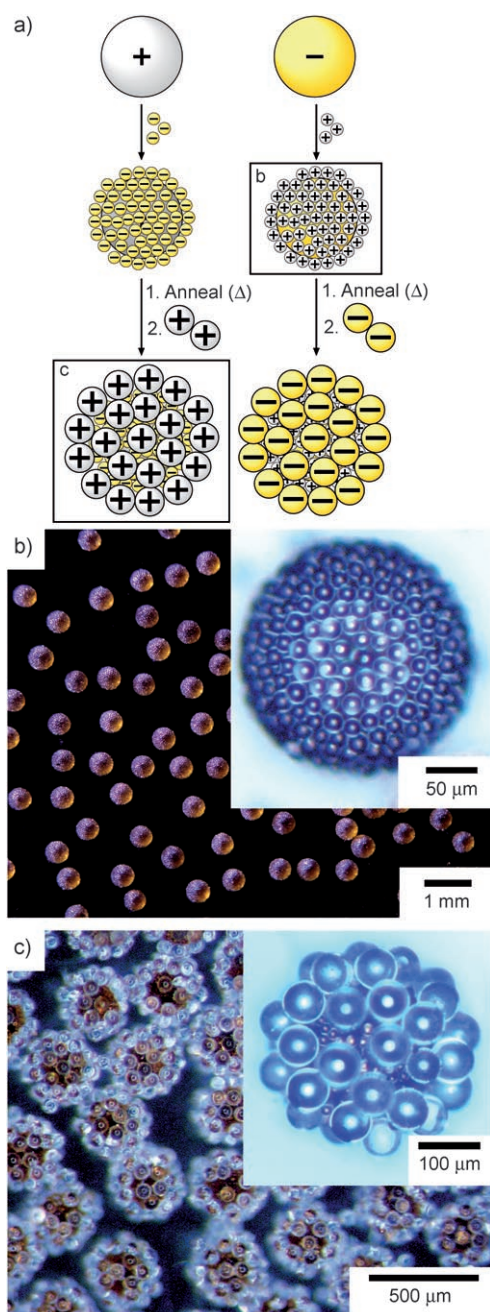The experiments shown schematically in Figure 4a demonstrate that the self-assembly is due to electrostatic inter-

Figure 3. a) A schematic representation of the procedure for multistep electrostatic self-assembly of charged polystyrene microspheres. b) Optical micrographs of the structures resulting from a combination of 200-μm-diameter negatively charged orange spheres with 20-μm-diameter positively charged colorless spheres. c) Optical micrographs of the structures resulting from the multistep self-assembly of 200-μm-diameter positively charged colorless spheres, 20-μm-diameter negatively charged orange spheres, and 70-μm-diameter positively charged colorless spheres. Note the small orange spheres visible in the gaps between the outermost spheres. See text for details. The images in (b) and (c) correspond to the boxed structures b and c, respectively, in (a).

actions. To a mixture of both positively charged (colorless) and negatively charged (orange) 200-μm-diameter spheres we added an excess of 20-μm-diameter positively charged (color-
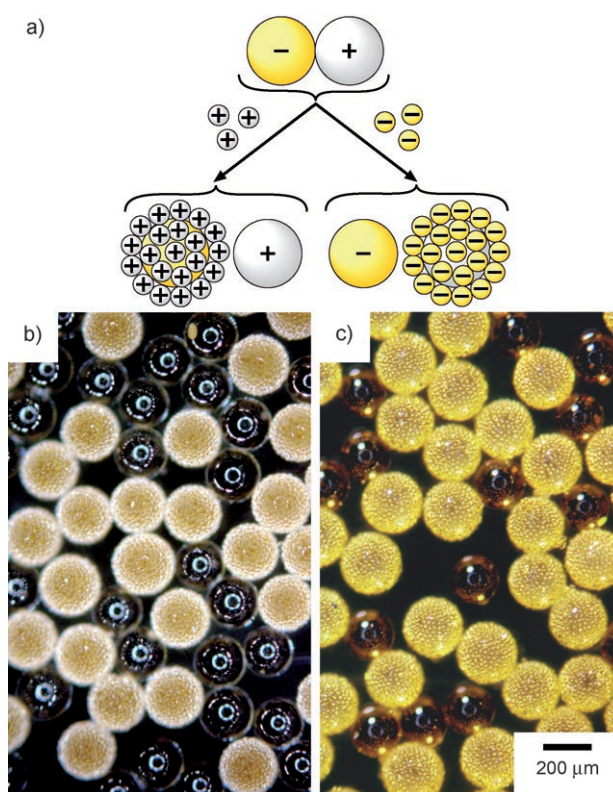

Figure 4. a) A schematic representation of the experiment demonstrating that assembly involves electrostatic interactions (see text for details). b) An optical micrograph of the assemblies resulting from a mixture of 200-μm-diameter positively charged colorless spheres, 200-μm-diameter negatively charged orange spheres, and 20-μm-diameter positively charged colorless spheres. c) An optical micrograph (on the same scale) of the assemblies resulting from a mixture of 200-μm-diameter positively charged colorless spheres, 200-μm-diameter negatively charged orange spheres, and 20-μm-diameter negatively charged orange spheres.

less) spheres. The small spheres coated only those large spheres with the opposite charge, while the like-charged spheres remained uncoated (Figure 4b). To a similar mixture of large spheres we added small negatively charged (orange) spheres. Again, the small spheres coated only those large spheres with the opposite charge (Figure 4c). We obtained the same results regardless of the order in which the three batches of spheres were combined. As an additional test, we gently agitated some of the self-assembled structures while exposing them to ionized air from an anti-static gun (Zerostat) and found that the structures disassembled into individual microspheres. Finally, we performed a control experiment in which we combined 200-μm and 20-μm unfunctionalized polystyrene beads under the same conditions used for the other assemblies. We observed almost no adhesion between these unfunctionalized beads (Figure S2 in the Supporting Information).

In conclusion, we used the ion-transfer model of contact electrification to design microspheres that develop predictable electrostatic charges upon contact with other surfaces. Oppositely charged microspheres self-assemble into uniform spherical microstructures. By using contact electrification to

produce charged components, we avoid the use of expensive equipment such as a high-voltage power supply or an electron-beam gun, and enable the use of large quantities of material, or assembly over large areas. Our assemblies form within seconds in greater than 99.9 % yield, and we can use the assembled structures as components in multistep self-assembly. We assemble dry particles in air, and can assemble particles as small as 5-μm in diameter. The use of dry self-assembly avoids the coagulation that can occur when a solid is isolated from a liquid suspension, but it limits the minimum particle size for this technique, as sub-1-μm dry powders tend to form extended aggregates. We speculate that this process could be used to encapsulate or coat microscale particles (e.g., for drug delivery), or to increase the accessible surface area of a solid support in a controlled fashion. Although we have demonstrated electrostatic charging and self-assembly only with polystyrene microspheres, any dielectric material that can be functionalized with covalently bound ions and mobile counterions should demonstrate similar charging properties.

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