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Introduction & Motivation

Vertically aligned one-dimensional (1D) architectures including nanotubes, nanorods, and nanowhiskers have been of growing interest due to potential applications in sensor, memory, and photovoltaic devices. In dye sensitized solar cells (DSSCs), for example, TiO2 nanotubes can provide direct pathways for electrons through the anode, reducing internal impedance and enhancing the charge collection efficiency. However, it has not been possible to grow nanotubes on transparent conducting oxide glass with the lengths needed for high-efficiency (tens of micrometers), and large areas desired for economy. In this case, vertical alignment of acicular micro particles may be preferable using a top-down approach.

We propose to utilize a microsphere lithography strategy to build 1D, hierarchical structures. A closely packed monolayer of glass microspheres can accommodate "stand-up" texture of acicular particles by occupying the interstitial sites. To our knowledge, the interaction between spheres and needles in the size range mm to um is unexplored. In the current work, we investigate the tendency of short (mm-size) wires to orient vertically in a monolayer of spheres using simple shaking action. This is a statistical study with the intention of identifying geometric matching of sphere and wire sizes.



Figure 1. DSSC containing glass microstructure with "stand-up" texture

Experimental Procedure

Plastic spheres, 8 and 6 mm diameter, and glass spheres, 3 mm and 2 mm, were used to create four distinct, close - packed monolayer models inside hexagonal-shaped, flat-bottomed containers.





Figure 2. Monolayer- 3mm spheres

Figure 3. Vibration apparatus

Vertical Orientation of Short Wires Using a Monolayer of Spheres

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Metallic needles with various diameters and lengths were chosen based on interstitial diameters. Each experiment used 50 needles and was run for one minute on a vibrational apparatus, and oriented needles were manually counted. Three replicates were performed, and the experimental data was analyzed with full factorial design (two factors, two or more than two levels) in Minitab with a confidence interval of 95%, α=0.05.

Table 1. Needle	size vs.	sphere	diameter

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Needle Diameter	Sphere Diameter		Needle Diameter	Sphere Diameter				
(µm)	8 mm	6 mm	(µm)	3 mm	2 mm			
1010	\checkmark	×	320	\checkmark	×			
710	\checkmark	\checkmark	200	\checkmark	\checkmark			
540	\checkmark	\checkmark	178	\checkmark	\checkmark			
320	\checkmark	\checkmark	160	\checkmark	\checkmark			
200	×	\checkmark	127	×	\checkmark			
178	×	\checkmark	×					
Length-12 10 8 and 6 mm		length-43 and 2 mm						



Figure 4. Orientation of wires (a) 3mm spheres (b) 2mm spheres

Conclusions and Plans

- The max. orientation window or "Sweet spot" decreases in size with decreasing sphere and particle size.
- Maximum orientation for macro particles appears to occur when L_{needle} $= \emptyset_{\text{sphere}}$. Optimal $\emptyset_{\text{needle}} / \emptyset_{\text{interstitial}}$ varies in the range of 0.25 - 0.5.
- Deviation from expected behavior occurs at $Ø_{sohere} = 2mm$, perhaps due to dominating surface forces over gravitational forces.
- Experiments are underway to produce titanate-based acicular particles in the sub-mm to micron size range for similar experiments with microspheres in order to determine the limits of this approach.
- Ultimately, we will build and test DSSCs with wide bandgap anodes with this unique architecture.

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 L_n : needle length, $Ø_s$: sphere diameter, $Ø_n$: needle diameter, $Ø_i$: interstitial diameter

Figures 5 – 8. Graphs representing upright needle orientation. (a) Contour plot as a function of needle size relative to monolayer sphere and interstitial size (b) Line plot as a function of needle size.

