

Big Nano Success Stories

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Many feel that nanotechnology has been severely overhyped - *big promise of small things, small results of big things*. But while we wait for that world-changing nano-event that's just around a quantum corner, we might be able to dig up some modest success stories. Let's begin at the surface, the skin, in fact, to discover how nanotech has been helping us stay safer (maybe) and look better (maybe). You may already know that some sun blocks use UV-absorbing TiO₂ white paint pigment as the high tech ingredient. Nano-sized TiO₂ particles don't reflect white light, but they block UV. So let's count this as a nano health breakthrough even though DuPont was making nano-TiO₂ about 70 years ago [1]. Some will say that nano-TiO₂ sun block is too simple, so here's another try. How about cosmetics and nano-particle colorants? It turns out that "make-up" formulators adopted nano-particle pigments even before the nano sun blocks appeared. When? How about a few thousand years ago. Egyptians used black eye shadow mixtures that are now known to contain nano-particles of galena, or lead sulfide. Galena crystals, that naturally form 5-nanometer particles, were also used as hair color by Romans and Greeks, as far back as 2400 BC. These nano-particles still reside in ancient hair samples.

Let's raise the bar and move to a higher tech level, like photonic filters - with no dyes or color pigments. Durable glass filters can be made with nano-particles to eliminate fading. Red glass is a superb example and it can be made using one of the darlings of the nano-world - nanogold. The beautiful red cathedral glass, and certain red cups, are a permanent red because of the optical effects of the nanogold particles. The long-mysterious Lycurgus Cup is a beautiful example of red glass that derives its transmitted red, but reflected green, from nanogold particles [2, 3]. Oops, how old is this technology? Well, it seems like nanogold has been around for quite a few centuries. The Lycurgus Cup is dated as 4th century AD. By the way, the cup depicts King Lycurgus being dragged into the underworld. Maybe there's a message here for the nano-hypsters and nano-pretenders.



FIG.1 - Lycurgus Cup

Now let's look at functional materials. Tiny carbon structures are a high-focus area for nanotechnology with thousands of articles appearing on carbon nanotubes, bucky balls (C₆₀), and graphene (single layer graphite). While we wait for breakthroughs like CNT ICs, let's look for simpler applications like carbon-based fillers. Nano-scale carbon can provide a major performance boost for polymers, but is it cost-effective? It's been discovered that rubber becomes much more durable, while retaining desirable properties, if right-sized carbon is added. The tire industry began adding nano-sized carbon filler in the 1920's to double tire life; they still do. Forget expensive CNTs, we need affordability. Carbon black works just fine and all you need is a sooty flame.

We've found some nano success stories, but they seem to predate the term "nanotechnology". Perhaps it's not fair to count nanotech successes that precede the terminology and all the government funding. These early technologists were probably just practicing accidental nanotech when they made these breakthroughs, anyway. So let's leave the easier realm of nano-particle additives and move to complex 3D nano-structures.

Imagine a low-cost nano-conversion process where the surface of ordinary metal could be changed into a tough, durable dielectric coating that might even be used as a high-thermal circuit substrate. The tough non-conductive surface would be comprised of a symmetrical array of nano-vias. These 20-nanometer diameter vias (let's call them nano-channels or nanotubes) are just the right size for trapping atoms and even larger molecules. The good news is that this nano-structure coating process has been demonstrated. Results suggest that it can be a well-controlled electrochemical process with great potential. What's more, nanoparticles can be loaded into these high-aspect ratio nanotubes using self-assembly. Each nanotube can be efficiently filled with a nano-particle. Although the particle can be a single atom, the most exciting results have been obtained with colorants, pigments designed to fit into the nanotubes. Once inside the nanotube, a size-changing process is used to reduce the nanotube diameter, and to permanently trap the nano-particle. This sequence of generating a nanotube surface, filling the tubes with nano-particles, and shrinking the tubes, produces a highly durable and colorful metal finish. And it can withstand harsh environments - almost indefinitely. Nano color coating is ready to go, and this is surely a nano breakthrough.

This breakthrough nano process is anodic coating that can be used on aluminum (and titanium). Figure 2 shows the surface structure. So why no excitement in the nano community? About 80 years ago, Martin Tosterud, a chemist for Alcoa, pioneered many of the nano-structuring and coloring processes now called *color anodizing* [4]. He understood that particles were being trapped inside of the tiny "pores". He probably knew that he was dealing in nanoscale dimensions, but that's not a big deal for chemists who operate in the sub-nano range. *While sufficiently advanced technology may be indistinguishable from magic, sufficiently advanced nanotechnology is indistinguishable from chemistry.*

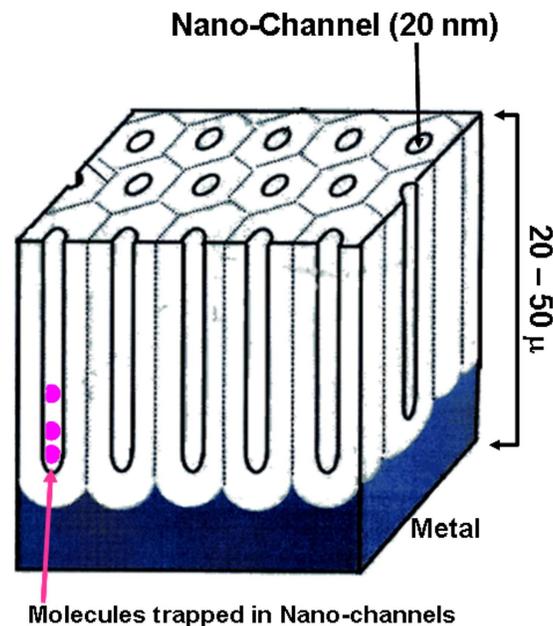


FIG. 2 - Aluminum oxide structure before the sealing step.

References

1. Peterson, J. H., "Titanium Dioxide Production", US Patent 2,448,683, filed in 1944.
2. Field, L., The Lycurgus Cup runneth over: Surface plasmon resonance in gold nanoparticles; www.physics.usyd.edu.au/pdfs/current/2005projects/LaurieField.pdf
3. Doremus, R. H., "Optical Properties of Small Gold Particles" (1964) J. Chem. Phys. 40 (8) at 2389.
4. Tosterud, M., "METHOD OF COLORING ALUMINUM", US Patent 1,965,269, filed in 1931.