# Sunscreen: A catch-22

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In classical times, wealthy people fortunate enough to stay indoors were pale and proud of it, while poor farmers and workers who toiled outdoors developed dark complexions from the sun's rays. People thus aspired to stay out of the sun and lived in a world relatively free of skin cancer. Yet today, we are constantly looking to become darker and acquire that "healthy glow" by increasing our exposure to the sun. This new trend has unfortunately arisen just as an already expanding hole threatens the ozone layer, and the prevalence of skin cancer is on the rise. However, we are confident that sunscreens can protect us from both the harmful short-term and long-term effects of the sun. Due to this sense of confidence we believe that as long as we repeatedly apply oils and lotions to our skin, the amount of time we spend in the sun is irrelevant. The question is if sunscreens in their present form are commonly accepted as the ultimate solution to the hazards of the sun, then why are more than one million new cases of skin cancer being reported each year?

Ultraviolet (UV) radiation is the type of solar radiation that is most threatening to our health. The most energetic UV radiation, UVC (100-280 nm wavelength), is almost entirely absorbed by the ozone layer and does not pose a threat to our skin. However, UVB and UVA radiation can penetrate the ozone layer and reach Earth's surface. UVB radiation (280-320 nm) is dangerous and carcinogenic due to its ability to directly mutate DNA. The least energetic UV radiation, UVA (320-400 nm), has also recently been recognized as dangerous due to its ability to indirectly damage our DNA via free radical-induced oxidation.[1] The high-energy UV radiation that reaches us can ultimately cause visible sunburn of the skin, erythema, photoaging, immunosupression, and photocarcinogenesis, among other adverse effects.[2] To prevent these adverse effects, sunscreens contain light-absorbing organic filters as well as light-reflecting and light-scattering inorganic nanoparticle filters. A combination of these two types of UV filters is necessary for broad-spectrum protection over the UVB and UVA ranges. However, these same protective compounds have been found to be either photoactive or photocatalytic when exposed to UV light with the potential to cause damage to our skin comparable to UV radiation alone. Each sunscreen product is thus a mixture of filters with known benefits and corresponding negative side effects.

The majority of organic UVB and UVA filters have their limitations. Many are photolabile: they can break down into a variety of harmful metabolites when they absorb UV light. PABA (para-aminobenzoic acid) was patented in 1943 and is known as a highly effective UVB absorber. However, it has been found to be photocarcinogenic.[3] Padimate A has been eliminated for its phototoxicity; oxybenzone is a broad-spectrum filter but is photolabile; butyl methoxydibenzoylmethane loses its photoprotection in a short period of time; octinoxate can improve the photostability of certain other filters but is a relatively weak absorber itself.[3] Recent studies have found that oxybenzones, cinnamates, salicylates, and their metabolites can significantly penetrate the skin. High levels of them were also detected in the blood and urine of human volunteer subjects.[4] The ability of these particles to enter our bloodstreams is particularly worrisome since they may have the potential to disrupt many bodily functions. The long-term effects of the penetration and breakdown

of these photolabile compounds found within sunscreens have yet to be determined with certainty.

The main inorganic or physical filters, titanium dioxide ($TiO_2$) and zinc oxide (ZnO), are photostable substances and depending on their size offer protection over a wide UV range. However, they are known photocatalysts: This means that UV light excites $TiO_2$ surface electrons to jump to higher energy levels leaving behind unstable positive holes in the $TiO_2$ lattice. Both the excited electrons and positive holes will react with nearby oxygen and hydrogen compounds ($O_2$, $OH^-$, etc.) to produce highly reactive free radical compounds including the superoxide anion radical ($O_2^{\bullet -}$) and the hydroxyl radical ($^{\bullet}OH$)[1]. When in contact with our skin, these radicals can oxidize and reduce compounds including DNA resulting in significant mutagenesis. In sunscreens, they can also interact with organic filters such as the benzoates to produce toxic acidic products.[1]

The potential solutions to this free radical damage include incorporating antioxidants such as carotenoids and vitamin C into sunscreens and coating inorganic filter particles with dimethicone, silica, or relatively photostable organic polymers.[4,5] Polymer coatings are translucent to allow UV radiation to reach the oxide particles so they can act as sunscreens. The coatings are also able to trap electrons in their structure and suppress the production and escape of free radicals from the particle surface.[5] Photocatalytic polymerization is a novel method for synthesizing polymer coatings on $TiO_2$ nanoparticles. This method takes advantage of the photocatalytic property of $TiO_2$ to induce polymerization and bond the polymer to the particle surface to form a surrounding protective lattice.

Another aspect of the sunscreen dilemma is our desire for an aesthetically pleasing product that can be rubbed onto the skin until it becomes translucent. In the past, products with $TiO_2$ and ZnO mainly contained these compounds at the microparticle size (~1 $\mu$m) and did not blend in with our skin. Recently, we have begun to incorporate much smaller $TiO_2$ and ZnO nanoparticles with diameters as small as 5-100 nm into sunscreens, because they become translucent when rubbed onto the skin. However, we have done this with no regard to the potential health risks. This societal trend unfortunately exacerbates the photocatalytic hazards of these particles since they have a significantly larger surface area to volume ratio for more photocatalysis [Figure 1]. In combination with these higher levels of photocatalysis, nanoparticles have a host of other characteristics that are intensified from their microparticle cousins. For one, their size allows them to penetrate the skin layer and individual skin cells more easily [Figure 2]. Nanotechnology research is new and ongoing, which means that there are little to no regulations on human exposure to these miniscule particles. Their long-term risks are not yet known and it is troubling that they are regularly incorporated into current commercial sunscreen products.

The effects of $TiO_2$ nanoparticle photocatalysis on individual molecules have been studied in several settings. Guanosine triphosphate (GTP), a common biomolecule, showed significant oxidative degradation over two hours when exposed to a suspension of $TiO_2$ nanoparticles and UVA/UVB radiation [Figure 1]. Research suggests that a polymer coating in this situation has the ability to inhibit photocatalytic GTP degradation by trapping free radicals [Figure 3].

The adverse effects of both the small size and photocatalytic activity of $TiO_2$ nanoparticles on the skin have also been explored in laboratory research. Human dermal fibroblasts (a type of skin cell) were studied and incubated with $TiO_2$ nanoparticles at concentrations well below the legal limit allowed

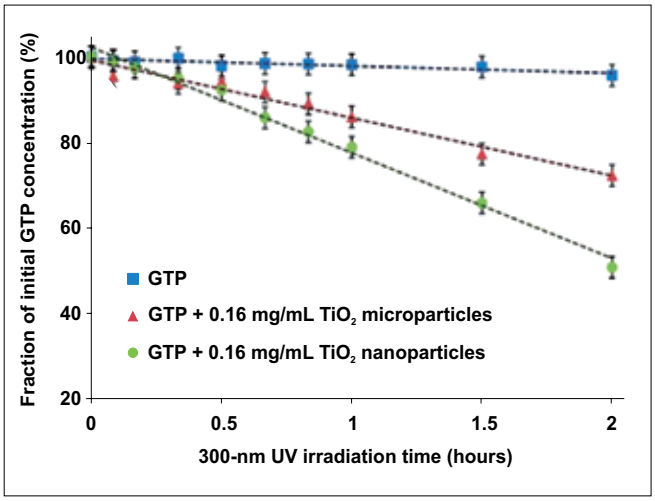


**Figure 1: Degradation of guanosine triphosphate (GTP) exposed to titanium dioxide particles and UV radiation. GTP is a common biomolecule used as a test subject to model the effects of $TiO_2$ photocatalysis. Microparticles cause 30% GTP degradation over two hours; <25 nm nanoparticles cause 50% GTP degradation over two hours due to greater surface area for photocatalysis. $TiO_2$ concentration of 0.16 mg/ml is well below the levels found in most sunscreens (research by authors)**

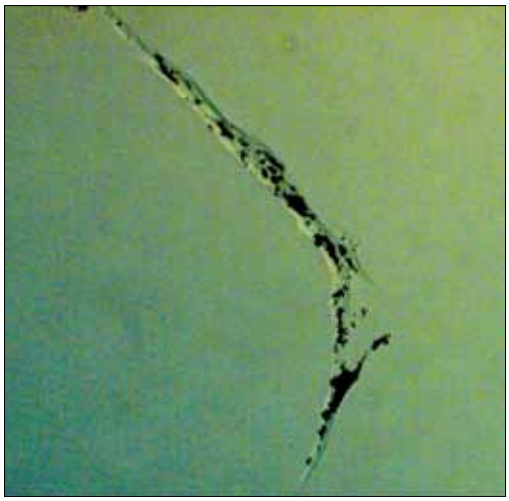

**Figure 2: Titanium dioxide nanoparticles penetrate the cell membrane of a human dermal fibroblast. <25 nm $TiO_2$ nanoparticles are able to infiltrate the membranes of human dermal fibroblasts, a type of skin cell, after 48 hours of cell incubation (research by authors)**

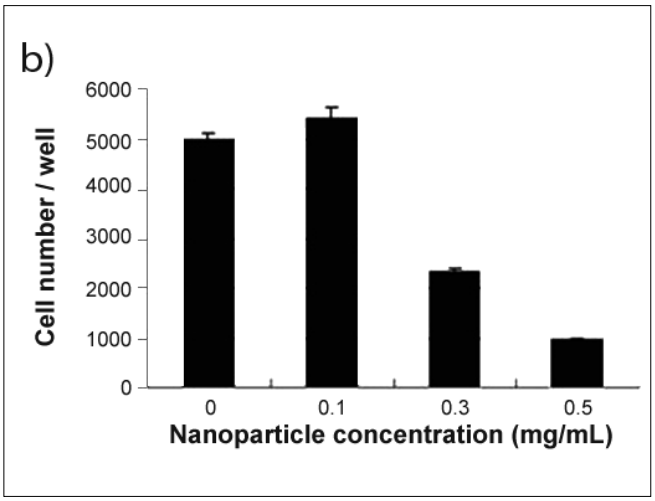


**Figure 4: Effect of titanium dioxide nanoparticle exposure on human dermal fibroblasts. Cell number after 3 days of incubation with $TiO_2$ nanoparticles at 0.1, 0.3 and 0.5 $mg \cdot mL^{-1}$. Increasing concentration of $TiO_2$ nanoparticles results in greater cell death (From Pan, Z. *et al.*, 2008)**

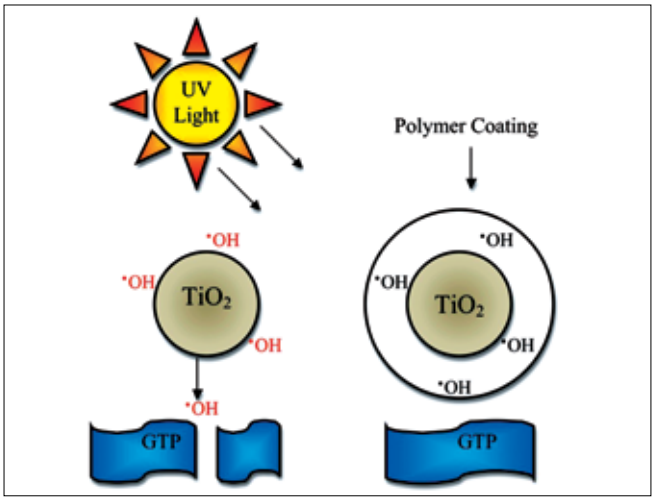


**Figure 3: Generalized model of the protective function of coating titanium dioxide nanoparticles with a biocompatible polymer. UV radiation stimulates photocatalysis on the surface of $TiO_2$ particles, leading to the production of highly oxidative free radicals that can damage our DNA. On left, uncoated $TiO_2$ photocatalysis leads to the destruction of GTP. On right, the polymer coating prevents free radicals from escaping the $TiO_2$ surface and damaging GTP**

in sunscreen products. In research by Zhi Pan and others, fibroblasts exposed to the nanoparticles exhibited decreased cell counts, decreased viability, and high levels of nanoparticles within the cell vesicles [Figure 4].[6] A sonochemical polymerization method, which has similar results to photocatalytic polymerization, was then used to graft a polymer coating onto the $TiO_2$ nanoparticles. Consequently, fibroblasts exposed to the polymer-coated nanoparticles were as healthy as control cells that were not exposed to nanoparticles [Figure 5]. These studies illustrate several harmful effects of $TiO_2$ nanoparticles commonly found in sunscreens and have given us some insight into polymer coating as a potential solution.

Perhaps the most disturbing fact in our search for the ultimate sunscreen is that we may never be able to test a product for long enough to rule out every potential side effect. Solar UV radiation alone and the photoactive and photolabile components of sunscreens are capable of destroying our genetic material and killing our skin cells, resulting in sunburn and carcinogenesis. However, carcinogenesis is not a result of the visible sunburn and does not result from the complete destruction of our genetic material. Carcinogenesis does occur when UV radiation damages our cells and DNA partially but not entirely, allowing the mutations to proliferate into future generations of deep skin cells. We can measure and predict these mutations on the immediate scale, but it is logistically and ethically impossible to accurately track the real long-term effects of UV radiation on skin tissue. Furthermore, we cannot create a study to account for every human variable (age, race, gender, complexion, exposure time, geographic location, etc.) while successfully tracking the proliferation of mutations over time.

After years of sunscreen research, we have many answers, but we are left with even more questions. We have learned that UVA radiation, which was

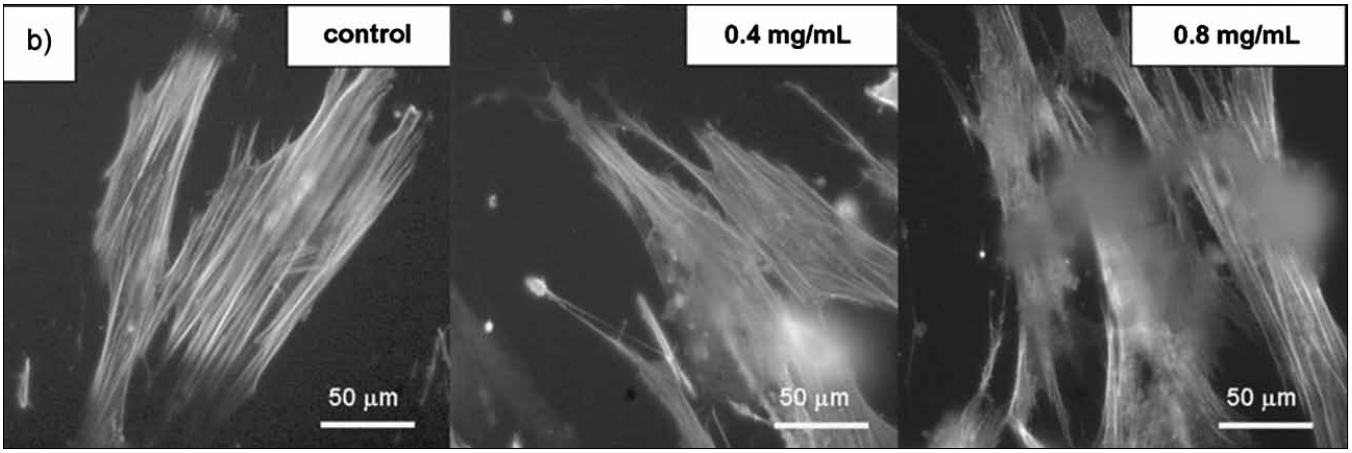


**Figure 5: Effect of polymer coated titanium dioxide nanoparticle exposure on human dermal fibroblasts. Confocal images of human dermal fibroblast cells incubated with polymer coated $TiO_2$ nanoparticles at 0.4 and 0.8 mg/mL. Cells incubated with coated nanoparticles are just as healthy as control cells, confirming that polymer coating can prevent nanoparticle penetration of the cell membrane and cell death**

once thought to be less damaging than UVB, has its own indirect mechanisms of damaging our DNA. "Broad-spectrum" protection now requires both organic and inorganic filters to block out all forms of significant UV radiation. We have also discovered that UV radiation can stimulate the breakdown of the organic filters and photocatalytic reactions in the inorganic filters in sunscreens. We have attempted to solve these problems with additives and alternatives such as polymer coating. Yet it is impossible to determine if these solutions will protect us from long-term UV exposure and will prevent the gradual proliferation of mutations that lead to deadly skin cancers. We do not know every precise mechanism in photocarcinogenesis and cannot confidently determine what truly causes skin cancer in an individual. So what then is the scientist's advice for the best protection from UV radiation? Wear a hat.

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