Titanium dioxide nanoparticle - Wikipedia

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Transmission electron micrograph of titanium dioxide nanoparticles from NIST Standard Reference Material 1898

Titanium dioxide nanoparticles, also called** ultrafine titanium dioxide** or** nanocrystalline titanium dioxide** or **microcrystalline titanium dioxide**, are particles of titanium dioxide (TiO2) with diameters less than 100 nm. Ultrafine TiO2 is used in sunscreens due to its ability to block UV radiation while remaining transparent on the skin. It is in rutile crystal structure and coated with silica or/and alumina to prevent photocatalytic phenomena. The health risks of ultrafine TiO2 from dermal exposure on intact skin are considered extremely low[1], and it is considered safer than other substances used for UV protection.

Ultrafine titanium dioxide has in anatase structure photocatalytic sterilizing properties, which make it useful as an additive in construction materials, for example in antifogging coatings and self-cleaning windows.

In the context of TiO2 production workers, inhalation exposure potentially presents a lung cancer risk, and standard hazard controls for nanomaterials are relevant for TiO2 nanoparticles.

Properties[edit]

Of the three common TiO2 polymorphs (crystal forms), TiO2 nanoparticles are produced in the rutile and anatase forms. Unlike larger TiO2 particles, TiO2 nanoparticles are transparent rather than white.Ultraviolet (UV) absorption characteristics are dependent from the crystal size of titanium dioxide and ultrafine particles has strong absorption against both UV-A (320–400 nm) and UV-B (280–320 nm) radiation[2]. Larger particles has almost no UV-absorption.

TiO2 nanoparticles have photocatalytic activity[3]:82[4] It is n-type semiconducter and its band gap between the valence and the conductivity bands is wider than of many other substances. The photocatalysis of TiO2 is a complex function of the physical characteristics of the particles. Doping TiO2 with certain atoms its photocatalytic activity could be enhanced.[5]

In contrast, pigment-grade TiO2 usually has a median particle size in the 200–300 nm range.[3]:1–2 Because TiO2 powders contain a range of sizes, they may have a fraction of nanoscale particles even if the average particle size is larger.[6] In turn ultafine particles usually form agglomerates and particle size could be much larger than crystal size.

Synthesis[edit]

Most manufactured nanoscale titanium dioxide is synthesized by the sulfate process, the chloride process or the sol-gel process.[7] In the sulfate process, anatase or rutile TiO_2 is produced by digesting ilmenite ($FeTiO_3$) or titanium slag with sulfuric acid. Ultrafine anatase form is precipitated from sulfate solution and ultrafine rutile from chloride solution.

In the chloride process, natural or synthetic rutile is chlorinated at temperatures of 850–1000 °C, and the titanium tetrachloride is converted to the ultafine anatase form by vapor-phase oxidation.[3]:1–2

It is not possible to convert pigmentary TiO_2 to ultrafine TiO_2 by grinding. Ultrafine titanium dioxide could be obtained by different kind of processes as precipitation method, gas-phase reaktion, sol-gel method, and atomic layer deposition method.

Uses[edit]

Ultrafine TiO_2 is believed to be one of the three most produced nanomaterials, along with silicon dioxide nanoparticles and zinc oxide nanoparticles.[6][8][9] It is the second most advertised nanomaterial in consumer products, behind silver nanoparticles.[10] Due to its long use as a commodity chemical, TiO_2 can be considered a “legacy nanomaterial.”[11][12]

Ultrafine TiO_2 is used in sunscreens due to its ability to block UV radiation while remaining transparent on the skin.[13] TiO_2 particles used in sunscreens typically have sizes in the range 5–50 nm.[2]

Ultrafine TiO_2 is used in housing and construction as an additive to paints, plastics, cements, windows, tiles, and other products for its UV absorption and photocatalytic sterilizing properties, for example in antifogging coatings and self-cleaning windows.[4] Engineered TiO_2 nanoparticles are also used in light-emitting diodes and solar cells.[3]:82 In addition, the photocatalytic activity of TiO_2 can be used to decompose organic compounds in wastewater.[2] TiO_2 nanoparticle products are sometimes coated with silica or alumina, or doped with another metal for specific applications.[3]:2[7]

Health and safety[edit]

Consumer[edit]

For sunscreens, health risk from dermal exposure on intact skin are considered extremely low, and is outweighed by the risk of ultraviolet radiation damageincluding cancer from not wearing sunscreen.[13] TiO_2 nanoparticles are considered safer than other substances used for UV protection.[4] However, there is concern that skin abrasions or rashes, or accidental ingestion of small amounts of sunscreen, are possible exposure pathways.[13] Cosmetics containing nanomaterials are not required to be labeled in the United States,[13] although they are in the European Union.[14]

Occupational[edit]

Inhalation exposure is the most common route of exposure to airborne particles in the workplace.[15] The U.S. National Institute for Occupational Safety and Health has classified inhaled ultrafine TiO_2 as a potential occupational carcinogen due to lung cancer risk in studies on rats, with a recommended exposure limit of 0.3 mg/m3 as a time-weighted average for up to 10 hr/day during a 40-hour work week. This is in contrast to fine TiO_2 (which has particle sizes below ~4 μm), which had insufficient evidence to classify as a potential occupational carcinogen, and has a higher recommended exposure limit of 2.4 mg/m3. The lung tumor response observed in rats exposed to ultrafine TiO_2 resulted from a secondary genotoxic mechanism related to the physical form of the inhaled particle, such as its surface area, rather than to the chemical compound itself, although there was insufficient evidence to corroborate this in humans.[3]:73–78 In addition, when finely dispersed in the air and in contact with a sufficiently strong ignition source, TiO_2 nanoparticles may present a dust explosionhazard.[4]

Standard controls and procedures for the health and safety hazards of nanomaterials are relevant for TiO_2 nanoparticles.[3]:82 Elimination and substitution, the most desirable approaches to hazard control, may be possible through choosing properties of the particle such as size, shape, functionalization, and agglomeration/aggregation state to improve their toxicological properties while retaining the desired functionality,[16] or by replacing a dry powder with a slurryor suspension in a liquid solvent to reduce dust exposure.[17][Engineering controls](/wiki/Engineering_controls), mainly ventilation systems such as fume hoods and gloveboxes, are the primary class of hazard controls on a day-to-day basis.[15][Administrative controls](/wiki/Administrative_controls) include training on best practices for safe handling, storage, and disposal of nanomaterials, proper labeling and warning signage, and encouraging a general safety culture.[17][Personal protective equipment](/wiki/Personal_protective_equipment) normally used for typical chemicals are also appropriate for nanomaterials, including long pants, long-sleeve shirts, closed-toed shoes, safety gloves, goggles, and impervious laboratory coats,[15] and in some circumstances respirators may be used.[16][Exposure assessment](/wiki/Exposure_assessment) methods include use of both particle counters, which monitor the real-time quantity of nanomaterials and other background particles; and filter-based samples, which can be used to identify the nanomaterial, usually using electron microscopy and elemental analysis.[16][18]

Environmental[edit]

Sunscreens containing TiO_2 nanoparticles can wash off into natural water bodies, and can enter wastewater when people shower.[6][13] Studies have indicated that TiO_2 nanoparticles can harm algae and animals and can bioaccumulate and bioconcentrate.[13] The U.S. Environmental

Protection Agencygenerally does not consider physical properties such as particle size in classifying substances, and regulates TiO_2 nanoparticles identically to other forms of TiO_2.[4]

Toxicity[edit]

Titanium dioxide has been found to be toxic to plants and small organisms such as worms, nematodes, and insects.[19] The toxicity of TiO_2 nanoparticles on nematodes increases with smaller nanoparticle diameter specifically 7 nm nanoparticles relative to 45 nm nanoparticles, but growth and reproduction are still affected regardless of the TiO_2 nanoparticle size.[19] The release of titanium dioxide into the soil can have a detrimental effect on the ecosystem in place due to its hindrance of proliferation and survival of soil invertebrates; it causes apoptosis as well as stunts growth, survival, and reproduction in these organisms. These invertebrates are responsible for the decomposition of organic matter and the progression of nutrient cycling in the surrounding ecosystem. Without the presence of these organisms, the soil composition would suffer.[19]

Metrology[edit]

ISO/TS 11937 is a metrology standard for measuring several characteristics of dry titanium dioxide powder relevant for nanotechnology: crystal structure and anatase–rutile ratio can be measured using X-ray diffraction, average particle and crystallite sizes using X-ray diffraction or transmission electron microscopy, and specific surface area using the Brunauer–Emmet–Teller gas adsorption method.[7][20] For workplace exposure assessment, NIOSH Method 0600 for mass concentration measurements of fine particles can be used for nanoparticles using an appropriate particle size-selective sampler, and if the size distribution is known then the surface area can be inferred from the mass measurement.[3]:79[21] NIOSH Method 7300 allows TiO_2 to be distinguished from other aerosols by elemental analysis using inductively coupled plasma atomic emission spectroscopy. Electron microscopy methods equipped with energy-dispersive X-ray spectroscopy can also identify the composition and size of particles.[3]:79[22]

NIST SRM 1898 is a reference material consisting of a dry powder of TiO_2 nanocrystals. It is intended as a benchmark in environmental or toxicological studies, and for calibrating instruments that measure specific surface area of nanomaterials by the Brunauer–Emmet–Teller method.[20][23][24][25]

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