

Giovanna Greco (2005-2008)
PhD in Bio-Chemical Sciences

Over the last two decades, there has been a very rapid implementation of nanotechnologies, which find practical applications in many fields of industry and daily life. Bio-nanotechnology and nanomedicine are dynamically developing fields of scientific interest and nanoparticles are studied as drug delivery systems in order to increase drug effectiveness and limit the side effects.

Concerns about human and environmental exposures resulting in potential adverse effects have increased as well.

Carbon nanotubes (CNTs) have been reported to elicit toxic responses both in vitro and in vivo, ascribed so far to metal contamination, CNT length, degree of oxidation, or extent of hydrophilicity. To examine how structural properties may modulate the toxicity of CNT, one preparation of multiwall CNT has been modified (i) by grinding (introducing structural defects) and subsequently heating either in a vacuum at 600 °C (causing reduction of oxygenated carbon functionalities and reduction of metallic oxides) or in an inert atmosphere at 2400 °C (causing elimination of metals and annealing of defects) and (ii) by heating at 2400 °C in an inert atmosphere and subsequently grinding the thermally treated CNT (introducing defects in a metal-deprived carbon framework). The presence of framework and surface defects, metals, and oxygenated functionalities was monitored by means of a set of techniques, including micro-Raman spectroscopy, adsorption calorimetry, X-ray photoelectron spectroscopy, inductively coupled plasma mass spectrometry, and atomic emission spectroscopy. Contrary to traditional toxicants, such as asbestos, CNT may quench rather than generate oxygenated free radicals. The potential of the modified CNT to scavenge hydroxyl radicals was thus evaluated by means of electron spin resonance spectroscopy (ESR/spin trapping).

The original ground material exhibited a scavenging activity toward hydroxyl radicals, which was eliminated by heating at 2400 °C but restored upon grinding. This scavenging activity, related to the presence of defects, appears to go paired with the genotoxic and inflammatory potential of CNT reported in the companion paper. Thus, defects may be one of the major factors governing the toxic potential of CNT.

Titania is generally considered to be an inert and safe material. Several studies, however, have reported that nanosized TiO₂ may elicit toxic effects. In some cases the observed adverse effects have been related to free radicals. TiO₂ nanoparticles hazard is associated to their photocatalytic activity causing release of DNA damaging ROS (Reactive Oxygen Species), lipid peroxidation and skin damage. Various coatings have been proposed to minimize photocatalysis, while keeping the potential to block UV radiations. Uncoated and variously coated commercial nano-titania have been classified on the basis of UVB-induced lipoperoxidation of linoleic acid. A selection of the most and the least protective specimens was

then examined by ESR (Electron Spin Resonance) to evidence the presence of surface paramagnetic centres and the release of ROS in aqueous suspensions (spin trapping). Paramagnetic centres and ROS were correlated with the extent of lipid peroxidation. When tested on porcine skin (mimicking the human one), titania acted as on linoleic acid. The combined use of lipid peroxidation of simple fatty acids with ESR analysis is here proposed as a possible screening tool for the evaluation of the potential toxicity of nano-titania in sunscreen preparations.

Although new studies mainly concern irradiated titania, the role and the mechanisms of the generation of free radicals by TiO_2 in the absence of UV irradiation are not well known. The purpose of the present study is to investigate the free-radical-generation mechanisms by nano- and micron-sized anatase or rutile powders under normal laboratory illumination or in the dark by means of a spin-trapping/ESR spectroscopy technique. This technique is used to identify the nature and the amount of free radicals released in solution, and in the solid-state to characterise the paramagnetic centres at the surface of particles that may participate in the reactions. The following radical-generating mechanisms have been considered:

1) the generation of oxygenated free radicals ($\text{HO}^{2\bullet}$, $\text{O}_2^{-\bullet}$, HO^\bullet) following the reaction of TiO_2 with oxygen, water or H_2O_2 and 2) the generation of carbon-centred radicals following the cleavage of the C-H bond in a model molecule. Although no free radicals were detected in a simply buffered solution, anatase and rutile generated O^{2-}

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and HO^\bullet , respectively, in the presence of H_2O_2 . Both polymorphs were also active in the cleavage of the C—H bond. Although the formation of O^{2-}

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→ appears to be related to exposure to sunlight, the generation of HO^\bullet and carbon-centred free radicals also occurs in the dark. When samples of equal surface area were tested, micron- and nanosized anatase was found to react in the same way indicating that a reduction in diameter does not generate new kinds of reactive sites. The data presented herein may have implications in the assessment of the health risk associated with the exposure to TiO_2

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nanoparticles and in the ecotoxicological impact following their possible leakage into the environment.