Airborne reactive oxygen species (ROS) is associated with nano TiO$_2$ concentrations in aerosolized cement particles during simulated work activities

Kiattisak Batsungnoen · Michael Riediker · Nancy B. Hopf · Guillaume Suárez

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Abstract Photocatalytic cement is self-cleaning due to the addition of titanium dioxide (TiO$_2$) nanoparticles, which react with sunlight (UV) and produce reactive oxygen species (ROS). Construction workers using photocatalytic cement are exposed not only to cement particles that are irritants but also to nano TiO$_2$ and UV, both carcinogens, as well as the generated ROS. Quantifying ROS generated from added nano TiO$_2$ in photocatalytic cement is necessary to efficiently assess combined health risks. We designed and built an experimental setup to generate, under controlled environmental conditions (i.e., temperature, relative humidity, UV irradiance), both regular and photocatalytic cement aerosols. In addition, cement working activities—namely bag emptying and concrete cutting—were simulated in an exposure chamber while continuously measuring particle size distribution/concentration with a scanning mobility particle sizer (SMPS). ROS production was measured with a newly developed photonic sensing system based on a colorimetric assay. ROS production generated from the photocatalytic cement aerosol exposed to UV ($3.3 \times 10^{-9}$ nmol/pt) was significantly higher than for regular cement aerosol, either UV-exposed ($0.5 \times 10^{-9}$ nmol/pt) or not ($1.1 \times 10^{-9}$ nmol/pt). Quantitatively, the level of photocatalytic activity measured for nano TiO$_2$-containing cement aerosol was in good agreement with the one obtained with only nano TiO$_2$ aerosol at similar experimental conditions of temperature and relative humidity (around 60%). As a consequence, we recommend that exposure reduction strategies, in addition to cement particle exposures, also consider nano TiO$_2$ and in situ–generated ROS, in particular if the work is done in sunny environments.

Keywords Photocatalytic cement · Nano cement · Nano TiO$_2$ exposure · Reactive oxygen species (ROS) · ROS exposure · Health effects
Introduction

Nanotechnology—the study of matter in nano range from 1 to 100 nm—is widely used to improve materials’ properties especially strength, weight, and insulation. In the construction sector, photocatalytic cement has been introduced for its self-cleaning properties (Lan et al. 2013; Carp et al. 2004; Banerjee et al. 2015) related to the photocatalytic activity of titanium dioxide nanoparticles (nano TiO₂) (Hernández-Rodríguez et al. 2019; Feng et al. 2013; Folli et al. 2010). This cement is composed of regular cement made up of fine inorganic particles such as CaO, SiO₂, Fe₂O₃, and MgO (Meo 2004; Batsungnoen et al. 2019) and nano TiO₂.

It is well-known that inhalation of particulate matter (PM) is associated with pulmonary and cardiovascular diseases (e.g., COPD, asthma, lung cancer) (Risom et al. 2005; Aust et al. 2002; Schins et al. 2004; Ghio and Devlin 2001; Knaapen et al. 2004; Upadhya et al. 2003; Upadhyay et al. 2003; Park et al. 2018). In addition, IARC has PM as a group 1 carcinogen (IARC 2017) and TiO₂ as possibly carcinogenic to humans (2B) (IARC 2015). Numerous studies have shown that nano TiO₂ is genotoxic and cytotoxic (NIOSH 2009; Sayes et al. 2006), especially for the lung bronchial epithelial cells (Sha et al. 2015; Lee et al. 2010) but can also translocate to other organs via the blood circulation (Wang et al. 2008; Kreyling et al. 2010; Geiser and Kreyling 2010; Shi et al. 2013).

Cell toxicity associated with nano TiO₂ exposure is related to reactive oxygen species (ROS) generation, which may lead to oxidative stress, lipid peroxidation, and nucleic acid alteration (Wang and Fan 2014; Shi et al. 2013; Panieri and Santoro 2016; Liou and Storz 2010). ROS such as hydroxyl radical, superoxide anion radical, hydrogen peroxide (H₂O₂), and singlet oxygen play a mechanistic role in many human diseases, including cancer (Waris and Ahsan 2006; Brieger et al. 2012), especially in the initiation and progression of multistage carcinogenesis (Waris and Ahsan 2006). Elevated ROS levels have also been associated with various inflammation-related human diseases (Alfadda and Sallam 2012).

ROS are also generated outside of the body, and has to be considered together with the endogenous ROS exposure generated through the metabolic response. Environmental ROS generation is especially relevant when airborne nano TiO₂ particulates are exposed to UV (Vernez et al. 2017). Due to its electronic energy band gap, nano TiO₂ behaves as a semi-conductor: UV-excited electrons (\( \bar{e} \)) reach the conductance band while a hole (\( h^+ \)) forms at the valence energy level. The resulting \( \bar{e}/h^+ \) pair reacts with molecular oxygen (O₂) and water giving rise to a series of ROS formation. They react readily with organic materials (e.g., bacteria and mold), giving them a particularly efficient biocide property (Li et al. 2014; Lan et al. 2013; Li 2004; Chen and Poon 2009; Lee et al. 2010).

Photocatalytic cement exposure among outdoor construction workers may thus have direct exposures to ROS as secondary airborne toxicant (exogenous ROS) from UV activation of nano TiO₂. Concentrations of exogenous ROS have not yet been assessed for these workers; consequently, potential health risks associated to this exposure are currently unknown.

Airborne ROS can be quantified using a photonic detection device that was developed at our laboratory and which relies on the formation of a colorimetric complex (Fe (III)-orange xylenol) due to the oxidation of the probe solution containing reduced iron form (Fe (II)) by ROS (Laulagnet et al. 2015). The use of multiscattering absorbance enhancement (MAE) strategy as photonic core principle for the device enabled sensitive ROS determination (Suárez et al. 2013, 2014).

The main objective of the present study was to quantify amount of ROS generated from airborne cement and photocatalytic particles at constant relative humidity of about 60% under controlled conditions:

i) Laboratory aerosolization with photocatalytic and regular cements equipped with a UV lamp;

ii) Exposure chamber setup where two construction activities (cement bag emptying and concrete cutting) were simulated with both cement types separately.

Material and methods

Materials Photocatalytic cement was obtained from ESSROC (TX-Active®, Italcementi group, Nazareth, US), while regular cement defined as Portland cement CEM I (CE number 266–043-4) was purchased from Jura cement (Wildegg, Switzerland). The ROS-detection reagent—so-called FOX solution—was freshly prepared by mixing ammonium iron (Fe (II)) sulfate (260 \( \mu \)M), xylenol orange (130 \( \mu \)M), and D-sorbitol
(100 mM) into sulfuric acid (25 mM). The solution was kept in a fumed glass flask (100 mL). UV exposure was achieved using a solar light simulator (LS-1000 Solar Simulator Solar Light Co., Glenside, PA, USA). Jet-nebulizer system (1-jet Collison Mesa Labs, Butler, NJ; USA) was used to maintain controlled aerosol humidity to 60%. The Ecolog TH1 device enabled monitoring of both temperature and humidity during the aerosol generation (ELPRO-BUCHS AG, Buchs, Switzerland). System airflows were monitored using digital mass flow meters (Vögtlin Instruments AG, flow technology, Aesch BL, Switzerland). Concrete was made by mixing cement and water (2:1). Concrete cutting was operated with a circular saw (diameter 230 mm) and at maximum rated speed (6600 RPM) (PWS 20-230 J, BOSCH, Leinfelden-Echterdingen, Germany).

Methods

Generation of cement aerosols Airborne particles of both photocatalytic and regular cements were generated using an aerosolization system previously described by Ding and Riediker 2015, 2016. Two grams of cement were loaded into a glass funnel and dry air blown upwards through the funnel with 2 L/min. The experimental setup is shown in Fig. 1.

Control of environmental conditions The airborne particles produced in the funnel were transported directly into a mixing chamber by shear force and mixed with humid air originated from a nebulizer. The nebulizer flow rate was 1.5 L/min, which maintained the relative humidity at 60%. Downstream, the aerosol was driven into the exposure cylinder where they were exposed to UV radiation for 2.7 min (average residence time in the cylinder). The UV radiation light source was equipped with solar UV filters to reproduce the UV-A and UV-B spectrum. The lamp produced an irradiance intensity of 785 W/m² in the cylinder, corresponding to 12 folds the terrestrial irradiance. The airborne particles exiting the cylinder were captured in an impinger (25 mL) filled with FOX solution (5 mL). Temperature and relative humidity were monitored continuously during the run.

Working activities Two construction activities, cement bag emptying and concrete cutting, were simulated in an exposure chamber (10 m³) with either photocatalytic or regular cement. Prior to the simulation activities, the ventilation system (80 m³/h) was running for 2 h in order to reduce background particles, and during simulation, the ventilation system was off. The operator simulating the construction activity wore a respirator (N100, P3, or FFP3), a chemical suit, nitrile gloves, goggles, safety shoes, and hearing protection. The bag emptying activity was performed by turning an open cement bag (25 kg) upside-down, pouring it into a plastic container (diameter × height, 60 × 40 cm), and shaking until the cement bag was empty. The concrete cutting activity was performed by using a circular saw for 10 s cutting a prepared concrete block (size 25 × 36 × 6 cm). The aerosolized cement particles were sampled in the operator’s breathing zone with an impinger (25 mL) containing FOX solution (5 mL) and operating at a flow rate of 0.5 L/min. Each experimental construction activity was repeated in triplicate by a single operator, as shown in Fig. 2.

ROS analysis ROS concentration—also defined as oxidative potential—was determined using a photonic system developed by our laboratory and based on multiscattering-enhanced absorbance strategy (Laulagnet et al. 2015; Vernez et al. 2017). In brief, air samples are bubbled through an impinger filled FOX solution (5 mL), which is the reaction medium. In the presence of ROS, the Fe (II) undergoes oxidized into Fe (III) that forms a complex with orange xyleneol absorbing light at 580 nm. The color change is measured via the use of a narrow emission led (580 nm) coupled to a photodetector both driven through a microcontroller board (Arduino Uno) The multiscattering regime occurring in the photonic cell due to the combination of rough aluminum cavity and inner Teflon housing enables dramatic lengthening of the optical path and improved analytical sensitivity. The ROS sensor response was calibrated with H₂O₂ and ROS values expressed as H₂O₂ equivalents.

Particles measurements The size distribution and number concentration of airborne nanoparticles in the size range between 11 and 1083 nm were measured by a scanning mobility particle sizer (SMPS) (model SMPS+ C model 5400, Grimm Aerosol Technik GmbH & Co. KG, Ainring, Germany). For morphology determination, the particles were collected onto Transmission Electron Microscopy (TEM) grids (Quantifoil R1/4, Quantifoil Micro Tools GmbH, Germany) using a mini particle sampler (MPS) (Ecomesure, Sacly, France).
operating at a sampling flow rate of 0.3 L/min. The TEM grids were transferred to a transmission electron microscope (TEM) (TEM CM-100 (JEOL, USA) at 80 kV).

Statistical analysis Means and standard deviations for nanoparticle size and distribution as well as ROS concentrations were compared by two-sample t test using STATA version 15.

Results

The ROS detection system developed by our group enabled us to quantify hydrogen peroxide (H$_2$O$_2$) and hydroxyl radicals (OH$^\cdot$). Quantitative determination of the aerosol reactivity expressed—once normalized by total particle number concentration—in nanomoles of H$_2$O$_2$ equivalents per particle (nmol/pt) was possible by combining accurate aerosol generation and sensitive ROS detection.

The average size distribution from aerosolized photocatalytic cement in the experimental setup was around $2 \times 10^5$ pt/cm$^3$, with a geometric mean diameter (GMD) of 285 nm and a geometric standard deviation (GSD) of 1.65 nm. Regular cement aerosol had a particle number concentration of $1 \times 10^5$ pt/cm$^3$ with GMD and GSD of 376 and 1.74 nm, respectively (Fig. 3a). The TEM images confirmed that photocatalytic cement aerosols contained agglomerates from pristine nanoparticles with primary size around 50 nm (Fig. 3b).

In complement, the aerosol ROS generation calculated in the present study indicates that the aerosolized
photocatalytic cement exposed to UV irradiance (3.3 \times 10^{-9} \text{ nmol/pt}) is significantly more reactive in terms of produced H\textsubscript{2}O\textsubscript{2} equivalents than regular cement exposed to UV (0.5 \times 10^{-9} \text{ nmol/pt}) or not (1.1 \times 10^{-9} \text{ nmol/pt}). ROS generation for non-UV-exposed cement aerosols were 1.6 \times 10^{-9} \text{ nmol/pt} and 1.1 \times 10^{-9} \text{ nmol/pt} for photocatalytic and regular cement, respectively (Table 1). In good agreement with a prior study (Vernez et al. 2017), the results herein obtained clearly indicate that the presence of nano TiO\textsubscript{2} in the photocatalytic cement do increase its chemical reactivity in terms of ROS generation prompt to act as secondary toxicants.

The effect of UV irradiance on nano TiO\textsubscript{2} is manifest in the fact that ROS generation from photocatalytic cement doubled in the presence of UV irradiance. As expected, ROS production from photocatalytic cement exposed to UV was significantly higher than regular cement with or without UV (Fig. 4). There was no significant difference in ROS generation between regular cement exposed and not to UV light.

Simulated construction work activities performed in exposure chamber to evaluate airborne ROS levels show that for bag emptying activity, the measured ROS production was significantly greater (p value = 0.04) for photocatalytic (4.6 \times 10^{-10} \text{ nmol/pt}) than for regular cement (1.5 \times 10^{-10} \text{ nmol/pt}) during bag emptying (Fig. 5). In the case of concrete cutting, no significant difference was observed between photocatalytic and regular cement, with ROS reactivities of 1.1 \times 10^{-10} and 1.1 \times 10^{-10} \text{ nmol/pt}, respectively (Table 2).

Discussion

Airborne photocatalytic cement particles are a potential source of ROS that is further enhanced in the presence of UV irradiance, and is mainly attributed to the presence of nano TiO\textsubscript{2} on the airborne particles (Batsungnoen et al. 2019). The photo-induced mechanism that triggers the production of ROS—mainly in the form of H\textsubscript{2}O\textsubscript{2}—at the surface of TiO\textsubscript{2} is well-established (Kakinoki et al. 2004, Ghadiry et al. 2016) and has recently been demonstrated for nano TiO\textsubscript{2} airborne particles in our prior study (Vernez et al. 2017). The results obtained herein clearly indicate that the presence of nano TiO\textsubscript{2} in the photocatalytic cement increase its chemical reactivity in terms of ROS generation, which is in good agreement with this prior study (Vernez et al. 2017).

In the absence of UV irradiance, the ROS generation associated to photocatalytic cement aerosol is not significantly different than the one obtained with regular cement, exposed or not. However, the large interval observed in the ROS production by photocatalytic aerosol without UV exposure might be attributed to the activation of nano TiO\textsubscript{2} by visible light during experimental measurements (Etacheri et al. 2015). Consequently, indoor construction workers using photocatalytic cement under artificial light might have greater exposures to ROS compared with workers using regular cement, although to a far lesser extent than outdoor workers.
The low reactivity observed with regular cement particles could potentially be originated from redox reactions in which transition metal in its composition—namely iron oxide (2% Fe₂O₃)—are prone to take part (Batsungnoen et al. 2019). While many studies have demonstrated the ability of iron oxides particles—such as Fe₂O₃ and to a greater extent Fe₃O₄—to activate H₂O₂ into highly reactive hydroxyl radical via their so-called peroxidase-like behavior (Gao et al. 2017; Pham et al. 2012), to our knowledge, the contribution of iron oxide in the generation of exogenous ROS by Portland cement particles was not yet reported.

In the case of work activities, the ROS production observed during bag emptying with photocatalytic cement was three-fold greater than the one measured with regular cement. Again, even in the absence of UV irradiance, this photocatalytic activity may be attributed to the visible light energy present in the experimental setup, though nano-TiO₂ can produce ROS also under dark conditions (Kakinoki et al. 2004). More

![Graph](image1)

**Fig. 3 (a)** Airborne nanoparticle size distribution expressed in number concentration (dN (/cm³)) obtained by SMPS for photocatalytic cement (solid circles) and regular cement (solid triangles) in the range size between 11 and 1083 nm. TEM images of (b) photocatalytic cement and (c) regular cement; (magnification, ×66,000)

|                          | ROS concentration (nmol/pt) | TiO₂ content (wt%) | Avg. particle concentration (pt/cm³) | Distribution interval (nm) |
|--------------------------|-----------------------------|-------------------|---------------------------------------|----------------------------|
| Photocatalytic cement exposed UV | 3.34·10⁻⁹ (SD = 1.32·10⁻⁹) | 37.35             | 214,482                               | 100–930                   |
| Photocatalytic cement non-exposed UV | 1.58·10⁻⁹ (SD = 0.11·10⁻⁹) | 37.35             | 182,996                               | 100–930                   |
| Average particle concentration (pt/cm³) | 198,739                     |                   |                                       |                            |
| Regular cement exposed UV    | 0.51·10⁻⁹ (SD = 0.20·10⁻⁹) | 0.16              | 139,132                               | 550–1000**                |
| Regular cement non-exposed UV | 1.12·10⁻⁹ (SD = 0.54·10⁻⁹) | 0.16              | 76,616                                | 550–1000**                |
| Average particle concentration (pt/cm³) | 107,874                     |                   |                                       |                            |

*From Batsungnoen et al. 2019

**Top range detection limit for SMPS measurements
interestingly, one can notice that in the case of concrete cutting no significant difference is shown between photocatalytic and regular concretes, while in parallel, the corresponding TiO$_2$ contents in the generated aerosols are relatively low (max. 2%) as shown in Table 2. The different TiO$_2$ content observed depending on the work activity is explained by the fact that bag emptying process favors the smaller size fraction to remain airborne (16.5% of TiO$_2$ detected airborne), while the larger cement powder particles will sediment rapidly. In contrast, aerosols created from cement concrete cutting roughly reflects the initial composition of the initial cement powder in the bag (2.0% nano TiO$_2$) because the TiO$_2$ has become part of the cement matrix and is no longer present as individual nano TiO$_2$ particles. It is worthily to notice that the ROS concentration measured during bag emptying using photocatalytic cement was in the same order of magnitude than the value obtained in

![Fig. 4](image1)

**Fig. 4** Box plot showing the normalized ROS production (nmol/pt) originated from photocatalytic and regular cement airborne particles

![Fig. 5](image2)

**Fig. 5** The ROS production from cement bag emptying and concrete cutting
prior work with pure nano TiO$_2$ once normalized by TiO$_2$ content (Vernez et al. 2017).

Finally, health effects related to airborne nano TiO$_2$ exposure in photocatalytic cement should integrate its reactivity—in the presence of environmental UV/vis irradiance—by considering the associated ROS products as secondary airborne toxicants. In terms of toxic effects, ROS are associated to various metabolic/pathological paths such as oxidative stress, inflammation, genotoxicity, cytotoxicity, DNA damage, and cancer (Li et al. 2014; Brieger et al. 2012; Scherz-Shouval and Elazar 2011; Jaeger et al. 2012; Yin et al. 2012; Jaeger et al. 2012; Wang and Fan 2014).

**Conclusion**

The combination of an efficient aerosol generation setup coupled with a solar simulation lamp and a sensitive photonic detection device made it possible to assess the production of ROS by photocatalytic and regular cement aerosols. As expected, the presence of nano TiO$_2$ in photocatalytic cement has a strong impact on the ability of the corresponding aerosol to produce exogenous airborne ROS in the presence of UV light. Moreover, the level of ROS generated during work activities was found to be linked to the amount of airborne nano TiO$_2$ present in the cement aerosol. Thus, concrete cutting activities appear to be considerably less problematic in terms of ROS production than bag emptying for which the nano TiO$_2$ content in the aerosol reaches 16%. Considering the photoactivity of aerosolized photocatalytic cement under UV irradiance and the high content of airborne nano TiO$_2$ generated during bag emptying, worker protection procedures should not only consider nano TiO$_2$ exposure but also its ability to produce ROS as secondary airborne potential toxicants. Providing the specific reactivity of its aerosol under environmental conditions, photocatalytic cement should not only be considered a novel promising material but also a potential new hazard in construction sites.

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**Compliance with ethical standards**

**Conflict of interest** The authors declare that they have no conflict of interest.

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**References**

Alfadda AA, Sallam RM (2012) Reactive oxygen species in health and disease [research article]. Biomed Res Int 2012:1–14. https://doi.org/10.1155/2012/936486

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**Table 2** ROS concentration originated from aerosols generated during cement bag emptying and concrete cutting activities

| Activity                          | ROS concentration (nmol/pt) | TiO$_2$ content (wt%) | Avg. particle concentration (pt/cm$^3$) | Distribution interval (nm) |
|----------------------------------|----------------------------|-----------------------|----------------------------------------|----------------------------|
| Photocatalytic cement bag emptying | $4.60 \cdot 10^{-10}$ (SD = $3.47 \cdot 10^{-10}$) | 16.46                 | 3715                                   | 240–1000*                 |
| Regular cement bag emptying      | $1.58 \cdot 10^{-10}$ (SD = $1.81 \cdot 10^{-10}$) | 0.19                  | 3662                                   | 240–1000*                 |
| Photocatalytic concrete cutting   | $1.10 \cdot 10^{-10}$ (SD = $1.09 \cdot 10^{-10}$) | 2.03                  | 10,549                                 | 150–1000*                 |
| Regular concrete cutting          | $1.12 \cdot 10^{-10}$ (SD = $1.01 \cdot 10^{-10}$) | 0.10                  | 19,143                                 | 150–1000*                 |

*Top range detection limit for SMPS measurements
Aust AE, Ball JC, Hu AA, Lighty JS, Smith KR, Straccia AM, Veranth JM, Young WC (2002) Particle characteristics responsible for effects on human lung epithelial cells. Res Rep Health Eff Inst 110:1–65 discussion 67-76.

Banerjee S, Dionysiou DD, Pillai SC (2015) Self-cleaning applications of TiO2 by photo-induced hydrophilicity and photocatalysis. Appl Catal B Environ 176–177:396–428. https://doi.org/10.1016/j.apcata.2015.03.058

Batsungnoen K, Hopf NB, Suárez G, Riediker M (2019) Characterization of nanoparticles in aerosolized photocatalytic and regular cement. Aerosol Sci Technol 53(5):540–548. https://doi.org/10.1080/02786862.2019.1578334

Brieger K, Schiavone S, Miller FJ, Krause K-H (2012) Reactive oxygen species: from health to disease. Swiss Med Wkly 142:w13659. https://doi.org/10.4441/smw.2012.13659

Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. Prog Solid State Chem 32(1–2):33–177. https://doi.org/10.1016/j.progsolidchem.2004.08.001

Chen J, Poorn G (2009) Photocatalytic construction and building materials: from fundamentals to applications. Build Environ 44(9):1899–1906. https://doi.org/10.1016/j.buildenv.2009.01.002

Ding Y, Riediker M (2015) A system to assess the stability of airborne nanoparticle agglomerates under aerodynamic shear. J Aerosol Sci 88:98–108. https://doi.org/10.1016/j.jaerosci.2015.06.001

Ding Y, Riediker M (2016) A system to create stable nanoparticle aerosols from nanopowders. JoVE 113:e54414–e54414. https://doi.org/10.3791/54414

Etacheri V, Di Valentini C, Schneider J, Bahnemann D, Pillai SC (2015) Visible-light activation of TiO2 photocatalysts: advances in theory and experiments. J Photochem Photobiol C: Photochem Rev 25:1–29. https://doi.org/10.1016/j.jphotochemrev.2015.08.003

Feng D, Xie N, Gong C, Leng Z, Xiao H, Li H, Shi X (2013) Portland cement paste modified by TiO2 nanoparticles: a microstructure perspective. Ind Eng Chem Res 52(33):11575–11582. https://doi.org/10.1021/ie4011595

Folli A, Pochard I, Nonat A, Jakobsen UH, Shepherd AM, Macphee DE (2010) Engineering photocatalytic cements: understanding TiO2 surface chemistry to control and modulate Photocatalytic performances. J Am Ceram Soc 93(10):3360–3369. https://doi.org/10.1111/j.1551-2916.2010.03838.x

Gao L, Fan K, Yan X (2017) Iron oxide nanozyme: a multifunctional enzyme mimetic for biomedical applications. Theranostics 7(13):3207–3227. https://doi.org/10.7150/thno.19738

Geiser M, Kreyling WG (2004) Reactive oxygen species of TiO2 by photo-induced hydrophilicity and photocatalysis. Appl Catal B Environ 176–177:396–428. https://doi.org/10.1016/j.apcata.2015.03.058

Ghadiri M, Gholami M, Choon Kong L, Wu Yi C, Ahmad H, Alias Y (2016) Nano-anatase TiO2 for high performance optical humidity sensing on chip. Sensors 16(1):39. https://doi.org/10.3390/s16010039

Ghio AJ, Devlin RB (2001) Inflammatory lung injury after bronchial instillation of air pollution particles. Am J Respir Crit Care Med 164(4):704–708. https://doi.org/10.1164/ajrccm.164.4.2011089

Hernández-Rodriguez MJ, Santana Rodriguez R, Darias R, González Díaz O, Pérez Luzardo JM, Doña Rodríguez JM, Pulido Melián E (2019) Effect of TiO2 addition on mortars: characterization and photoactivity. Appl Sci 9(13):2598. https://doi.org/10.3390/app9132598

IARC (2015) Agents classified by the IARC monographs. World Health Organization, International Agency for Research on Cancer, vol 1–114. http://monographs.iarc.fr/ENG/Classification/

IARC (2017) IARC Monographs on the evaluation of carcinogenic risk to humans. IARC Monographs. WHO Press, Lyon. http://monographs.iarc.fr/ENG/Classification/latest_classif.php

Jaeger A, Weiss DG, Jonas L, Kriehuber R (2012) Oxidative stress-induced cytotoxic and genotoxic effects of nano-sized titanium dioxide particles in human HaCaT keratinocytes. Toxicology 296(1):27–36. https://doi.org/10.1016/j.tox.2012.02.016

Kakinoki K, Yamane K, Teraoka R, Otsuka M, Matsuoka Y (2004) Effect of relative humidity on the Photocatalytic activity of titanium dioxide and photoactivity of famotidine. J Pharm Sci 93(3):582–589. https://doi.org/10.1002/jps.10575

Knaapen AM, Borm PJA, Albrecht C, Schins RPF (2004) Inhaled particles and lung cancer. Part A: mechanisms. Int J Cancer 109(6):799–809. https://doi.org/10.1002/ijc.11708

Kreyling WG, Him S, Schleh C (2010) Nanoparticles in the lung. Nat Biotechnol 28(12):1275–1276. https://doi.org/10.1038/nbt.1735

Lan Y, Lu Y, Ren Z (2013) Mini review on photocatalysis of titanium dioxide nanoparticles and their solar applications. Nano Energy 2(5):1031–1045. https://doi.org/10.1016/j.nanoen.2013.04.002

Laulagnet A, Sauvain JJ, Concha-Lozano N, Riediker M, Suárez G (2015) Sensitive photonic system to measure oxidative potential of airborne nanoparticles and ROS levels in exhaled air. Procedia Eng 120:632–636. https://doi.org/10.1016/j.proeng.2015.08.659

Lee J, Mahendra S, Alvarez PJJ (2010) Nanomaterials in the construction industry: a review of their applications and environmental health and safety considerations. ACS Nano 4(7):3580–3590. https://doi.org/10.1021/nn100866w

Li G (2004) Properties of high-volume fly ash concrete incorporating nano-SiO2. Cem Concr Res 34(6):1043–1049. https://doi.org/10.1016/j.cemconres.2003.11.013

Li M, Yin J-J, Warner WG, Lo YM (2014) Mechanistic characterization of titanium dioxide nanoparticle-induced toxicity using electron spin resonance. J Food Drug Anal 22(1):76–85. https://doi.org/10.1016/j.jfda.2014.01.006

Liu G-Y, Storz P (2010) Reactive oxygen species in cancer. Free Radic Res 44(5):479–496. https://doi.org/10.3109/10715761003667554

Meo SA (2004) Health hazards of cement dust. Saudi Med J 25(9):1153–1159

NIOSH (2009) Approaches to safe nanotechnology managing the health and safety concerns associated with engineered nanomaterials. U.S. Department of Health and Human Services, Centers for Disease Control and Prevention, National Institute for Occupational Safety and Health. DHHS (NIOSH) Publication 2009:125.http://www.cdc.gov/niosh/docs/2009-125.pdf

Panieri E, Santoro MM (2016) ROS homeostasis and metabolism: a dangerous liaison in cancer cells. Cell Death Dis 7(6):e2253. https://doi.org/10.1038/cddis.2016.105
Park J, Park EH, Schauer JJ, Yi S-M, Heo J (2018) Reactive oxygen species (ROS) activity of ambient fine particles (PM2.5) measured in Seoul, Korea. Environ Int 117:276–283. https://doi.org/10.1016/j.envint.2018.05.018

Pham AL-T, Doyle FM, Sedlak DL (2012) Kinetics and efficiency of H2O2 activation by iron-containing minerals and aquifer materials. Water Res 46(19):6454–6462. https://doi.org/10.1016/j.watres.2012.09.020

Risom L, Møller P, Loft S (2005) Oxidative stress-induced DNA damage by particulate air pollution. Mutat Res 592(1):119–137. https://doi.org/10.1016/j.mrfmmm.2005.06.012

Sayes CM, Wahi R, Kurian PA, Liu Y, West JL, Ausman KD, Warheit DB, Colvin VL (2006) Correlating nanoscale titania structure with toxicity: a cytotoxicity and inflammatory response study with human dermal fibroblasts and human lung epithelial cells. Toxicol Sci 92(1):174–185. https://doi.org/10.1093/toxsci/kfj197

Scherz-Shouval R, Elazar Z (2011) Regulation of autophagy by ROS: physiology and pathology. Trends Biochem Sci 36(1):30–38. https://doi.org/10.1016/j.tibs.2010.07.007

Schins RPF, Lightbody JH, Born PJA, Shi T, Donaldson K, Stone V (2004) Inflammatory effects of coarse and fine particulate matter in relation to chemical and biological constituents. Toxicol Appl Pharmacol 195(1):1–11. https://doi.org/10.1016/j.taap.2003.10.002

Sha B, Gao W, Cui X, Wang L, Xu F (2015) The potential health challenges of TiO2 nanomaterials. J Appl Toxicol 35:1086–1101. https://doi.org/10.1002/jat.3193

Shi H, Magaye V, Castranova V, Zhao J (2013) Titanium dioxide nanoparticles: a review of current toxicological data. Particle Fibre Toxicol 10:15. https://doi.org/10.1186/1743-8977-10-15

Suárez G, Santschi C, Plateel G, Martin OF, Riediker M (2014) Absorbance enhancement in microplate wells for improved-sensitivity biosensors. Biosens Bioelectron 56:198–203. https://doi.org/10.1016/j.bios.2013.12.063

Suárez G, Santschi C, Slaveykova VI, Martin OF (2013) Sensing the dynamics of oxidative stress using enhanced absorption in protein-loaded random media. Sci Rep 3:3447. https://doi.org/10.1038/srep03447

Upadhyay D, Panduri V, Ghio A, Kamp DW (2003) Particulate matter induces alveolar epithelial cell DNA damage and apoptosis. Am J Respir Cell Mol Biol 29(2):180–187. https://doi.org/10.1165/rcmb.2002-0269OC

Vernez D, Sauvain J-J, Laulagnet A, Otaño AP, Hopf NB, Batsungnoen K, Suárez G (2017) Airborne nano-TiO2 particles: an innate or environmentally-induced toxicity? J Photochem Photobiol A Chem 343:119–125. https://doi.org/10.1016/j.jphotochem.2017.04.022

Wang J, Chen C, Liu Y, Jiao F, Li W, Lao F, Li Y, Li B, Ge C, Zhou G, Gao Y, Zhao Y, Chai Z (2008) Potential neurological lesion after nasal instillation of TiO2 nanoparticles in the anatase and rutile crystal phases. Toxicol Lett 183(1–3):72–80. https://doi.org/10.1016/j.toxlet.2008.10.001

Wang J, Fan Y (2014) Lung injury induced by TiO2 nanoparticles depends on their structural features: size, shape, crystal phases, and surface coating. Int J Mol Sci 15(12):22258–22278. https://doi.org/10.3390/ijms151222258

Waris G, Ahsan H (2006) Reactive oxygen species: role in the development of cancer and various chronic conditions. J Carcinogenesis 5:14. https://doi.org/10.1186/1477-3163-5-14

Yin J-J, Liu J, Ehrenshaft M, Roberts JE, Fu PP, Mason RP, Zhao B (2012) Phototoxicity of nano titanium dioxides in HaCaT keratinocytes—generation of reactive oxygen species and cell damage. Toxicol Appl Pharmacol 263(1):81–88. https://doi.org/10.1016/j.taap.2012.06.001

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