Photocatalytic oxide films in the built environment

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Abstract. The possibility to increase human comfort in buildings is a powerful driving force for the introduction of new technology. Among other things our sense of comfort depends on air quality, temperature, lighting level, and the possibility of having visual contact between indoors and outdoors. Indeed there is an intimate connection between energy, comfort, and health issues in the built environment, leading to a need for intelligent building materials and green architecture. Photocatalytic materials can be applied as coatings, filters, and be embedded in building materials to provide self-cleaning, antibacterial, air cleaning, deodorizing, and water cleaning functions utilizing either solar light or artificial illumination sources – either already present in buildings, or by purposefully designed luminaries. Huge improvements in indoor comfort can thus be made, and also alleviate negative health effects associated with buildings, such as the sick-house syndrome. At the same time huge cost savings can be made by reducing maintenance costs. Photocatalytic oxides can be chemically modified by changing their acid-base surface properties, which can be used to overcome deactivation problems commonly encountered for TiO₂ in air cleaning applications. In addition, the wetting properties of oxides can be tailored by surface chemical modifications and thus be made e.g. oleophobic and water repellent. Here we show results of surface acid modified TiO₂ coatings on various substrates by means of photo-fixation of surface sulfate species by a method invented in our group. In particular, we show that such surface treatments of photocatalytic concrete made by mixing TiO₂ nanoparticles in reactive concrete powders result in concrete surfaces with beneficial self-cleaning properties. We propose that such approaches are feasible for a number of applications in the built environment, including glass, tiles, sheet metals, plastics, etc.

1. Introduction
World-wide, 30-40% of all primary energy is used in buildings and up to 40% of greenhouse gas emissions come from the building sector, mostly from energy use during the lifetime of buildings [1]. Here, new materials have an important role for future green buildings and for upgrading today’s buildings. These materials can be used in a number of devices and in new coating technologies that can be integrated or added into the built environment. Proof-of-concepts have already been demonstrated or even commercialized in a few cases. Examples include controlling the input of visible light and solar energy in smart windows, pollutant abatement of urban (outdoor) air via photocatalysis occurring on exterior building surfaces, self-cleaning surfaces that avoid build-up of contaminants and hence reduces maintenance costs, daylight through light piping systems, hot water or warm air via selective absorption in solar collectors, electricity through building-integrated solar cells, providing coolness via infrared-selective emission towards the clear (night) sky, demand-controlled ventilation by the use of air quality sensors, phase change materials as heat sink and source in construction
elements, and superior thermal insulation via nanomaterials (aerogels) based vacuum panels. Materials for these applications have many features in common, not only regarding applications area but also materials types, and are now appearing as an international research field with strong internal cohesion [2].

Energy, comfort and health in the built environment are intimately connected. It is well documented that indoor air quality deterioration is due to occurrence of a large number of chemicals, or classes of chemicals. Among the most important categories of chemicals that occur in the indoor air are volatile organic compounds (VOC). The most commonly found are BTXS (benzene, toluene, xylenes and styrene), terpenes (α-pinene, limonene, etc.) and carbonyls (formaldehyde, acetaldehyde, and acetone). They originate from an increasing number of household products, electronic devices, and synthetic building materials. Simultaneously, changes in building design devised to improve energy efficiency have meant that modern homes and offices are frequently more air-tight than older structures. Whilst these improvements have led to more comfortable buildings with lower running costs, they also provide indoor environments in which contaminants are readily produced and may build up to much higher concentrations than those found outside. Recent reports indicate that adverse health effects are intimately linked to ventilation rates in buildings, although the literature does not provide clear evidence on particular agent(s) for the effects. The limited available data suggest that inflammation, respiratory infections, asthma symptoms and short-term sick leave increase with lower ventilation rates. Home ventilation rates above 0.5 air changes per hour have been shown to be linked to a reduced risk of allergic manifestations among children in a Nordic climate [3]. Higher ventilation rates in offices, up to about 25 l/s per person, are associated with reduced prevalence of sick building syndrome (SBS) symptoms. However, air ventilation is not unproblematic and may be unwanted. It requires energy supply in the heating, cooling, and ventilation (HVAC) system to warm/cool the fresh air, which scales with ventilation rate, and may also cause discomfort.

Surfaces that repel or decompose contaminants such as dirt particles, organic or inorganic molecules or even bacteria, without the need of external labor force or by the use of decontamination agents, are considered to be self-cleaning or easy-clean. It is a concept that has been introduced into different applications in which maintenance free surfaces are desirable [4, 5]. Broadly speaking, and by no means exhaustive, the self-cleaning effect can be divided into three main categories depending on the mechanism by which they operate. These are: (i) Hydrophilic or hydrophobic surfaces, whereby the wetting properties primarily are modified by surface structuring [4], (ii) photocatalytic surfaces where highly oxidizing species attack pollutants and ultimately convert them into CO₂, H₂O and mineral acids aided by light irradiation (preferably sun or indoor air illumination if it is to be a “self-cleaning” action) [5], (iii) surface charging or modification of chemical interactions and surface acid/base properties [6, 7]. Here we present a combination of the latter two strategies for cement surfaces following an approach we recently have demonstrated for TiO₂ thin films on glass substrates, namely surface modification by means of photo-fixation of SO₂ leading to acidic sulfate moieties. These were found to exhibit oleophobic or dirt repellent properties as probed by the adherence of a fatty acid [8, 9]. In particular, we show results of beneficial wetting and photocatalytic properties of reactive powder concrete samples with added TiO₂ nanoparticles at various concentrations up to 5 wt% TiO₂.

2. Materials and methods
Concrete samples with various concentrations (0, 1, 3 and 5 wt%) of TiO₂ pigment (Aeroxide P25, Evonik Industries AG) were made by mixing the pigment with reactive powder concrete. The following commercially available materials were used in the concrete sample manufacturing: Nanodur 5941 (Dykerhoff), undensified silica fume (Elkem), Limus 25 (Nordkalk). Glenium ACE (BASF). The amount of Nanodur was adjusted according to replacement level of Aeroxide P25 TiO₂ powders. The use of high performance and ultrahigh performance concrete require the use of large amounts of filler material (size < 125 μm), a low water to cement ratio (w/c) and higher amounts of super-plasticcer (SP) than in regular concretes. The w/c ratios can be very low, in the range of 0.18 - 0.25. This requires a
different mixing method and duration compared to standard methods, in particular more vigorous and longer periods of mixing. Here, a 1 liter Hobart paddle mixer set at speed “1” was used for the entire mixing sequence. After mixing the dry ingredients, water was added and further mixing was done for 1 min at speed “1”. The entire amount of SP was subsequently added and mixing was continued until the dry mass turns into a paste. Rheology measurements of the paste were performed to ensure that it meets the required consistency. The paste was then allowed to “rest”, i.e. allow air bubbles to escape from the paste. The paste was cast into standard prism forms (160 mm × 40 mm × 40 mm), and vibrated. The final casted concrete sample were finally covered with plastic and placed in a moist atmosphere at 20 °C.

Samples for further photocatalytic and self-cleaning measurements with dimensions 40 × 40 × 3 mm thick were cut from the concrete cast and polished to obtain a smooth surface. All samples were then left to be equilibrated 50 days in air after manufacturing before further processing. Prior to use all samples were then heated in air at 150°C for 1 h to remove excess water from the manufacturing and then kept in air at room temperature for 1 day before they were used in experiments.

The concrete samples were surface functionalized by means of photo-fixation of SO2 according to a method which has been described elsewhere [8, 9]. Briefly, the samples were heated to 150°C for 1 h in a gas mixture of air and 50 ppm SO2 and simultaneously irradiated with UV-A light (λ = 375 nm). This procedure produces SO2 bonded to oxygen vacancy sites, which after protonation in air yields sulfate terminated TiO2 surfaces with acidic properties [8, 10]. Figure 1 shows a photograph of the setup used for surface functionalization in this study which allows for functionalization of samples of the order 10 cm × 10 cm.

A photocatalyst indicator ink, resazurin (Rz), was used for the rapid assessment of the photocatalytic activity of the concrete samples [11, 12]. It is a commonly used oxidation-reduction indicator in e.g. cell viability assays and as pH indicator, and commercially available as sodium salt. The Rz ink is blue as prepared and irreversibly turns into the pink colored resorufin (Rf) under chemical reduction due to photo-induced reactions (figure 2). In our case the photo-reduction occurs via electron transfer from TiO2 irradiated with light larger than the band gap, $E_{g}$, of anatase TiO2, i.e. $E_{g} > 3.2$ eV, or $\lambda < 388$ nm).
A thin layer of 0.09 wt% Rz ink in deionized water (Ink Intelligent Ltd., Belfast, United Kingdom) was applied onto the concrete samples using a K-bar, and subsequently dried in air and dark conditions for 24 h. Digital photos of the samples were taken prior to irradiation. The samples were then irradiated with UV-A light (λ = 365 nm, ~10 mW cm⁻²) for 20 sec, and again photographed. Repeated cycles of UV-A irradiation and photography were performed for a total of 14 min irradiation time, thus yielding a time series of images capturing the photo-induced reactions of the Rz ink on the concrete surfaces. Image analysis was done with the software ImageJ to extract the RGB (red, green and blue) values from the image files. RGB data extraction was carried out on the same sample position with the same number of image pixels for all samples and image series. The blue signal decreases and the red signal increases as the Rz is reduced.

The wetting properties of the concrete samples were acquired by measuring the contact angle of applied droplet of water onto the surface of the samples employing an optical contact-measuring device (OCA15EC, DataPhysics Instruments GmbH, Filderstadt, Germany). The device is equipped with a CCD camera, an automatized syringe control system, and image analysis software. Droplets of water with 5 μl volume were applied onto the surface of the samples by the sessile drop method and digital images were acquired from the top and horizontal view, respectively. A rinsing test was also performed with the samples kept at an angle of 45° to study how water was removed from the surface, as the droplet slides along the tilted surface. In these latter experiments two concrete samples were used: one containing 5 wt% TiO₂ and one which had been further functionalized as described above. In each case 20 μl of water droplets were applied onto the surfaces and images were recorded when the drops reached the end of the samples.

3. Results and discussion
3.1. Photocatalytic activity measurements
Figure 3 shows results from photocatalytic activity test on pure and surface functionalized (S) concrete samples containing 0, 1, 3 and 5 wt% TiO₂. The columns marked “No UV” is photographs before UV-A irradiation, and the columns marked with “UV” depict samples that have been irradiated with UV-A light for 14 min, after which a pink colored areas emerge on samples denoted 1; 1,S; 3; 3,S; 5; and 5,S, respectively. The pink color signals that the samples are photocatalytic active and capable of reducing Rz upon UV-A irradiation. The pure samples (0 and 0,S) show no visible pink color, which indicates that it is the addition of TiO₂ which makes the samples photo-active. Similarly, by inspection of figure 3, it follows that TiO₂ particles are not evenly distributed on the substrate surfaces.

Figure 4 shows the results obtained from the RGB image analysis extraction process performed on the same set of samples as those shown in figure 3. The data are presented as normalized B and R values as a function of UV-A irradiation time. For each data set the R and B values were subtracted by the value at time t = 0, i.e. the initial color of the sample without irradiation to be able to make intersample comparisons of the relative color change. It is seen in figure 4 that initially the blue color rapidly increases and that the red color simultaneously decreases during the first few irradiation cycles, depending on sample type.
Figure 3. Resazurin dye photocatalytic activity test on pure and surface functionalized (S) concrete samples containing 0, 1, 3 and 5 wt% TiO₂. The samples were irradiated with UV-A light and a total irradiation time of 14 min. Resazurin changes color from blue to pink upon reduction, which is clearly visible on samples containing TiO₂ at concentrations >1 wt% (right panels).

We attribute this to the basic surface properties of the dried concrete samples and the pH sensitivity of Rz, as the concrete surface gradually is re-hydroxylated after the surface functionalization procedure. After extended UV-A irradiation (> 3-5 cycles) the red (blue) color starts to increase (decrease), which shows that the irreversible TiO₂-mediated photo-reduction of Rz to Rf occurs and is the dominant reaction pathway for Rz. The RB-values for both pure and surface functionalized samples with additions of 1, 3 and 5 wt% TiO₂ follow the same trend. The change of the R and B values for the sample 1,S is much smaller than sample 1 without surface functionalization. The difference in RB-values between samples with and without surface functionalization becomes very small at 3 wt% TiO₂, and becomes negligible or even reverse at 5 wt% TiO₂.

This suggests that the photocatalytic activity increases with TiO₂ concentration and that the surface functionalization does not inhibit the activity at high enough TiO₂ concentration (≥ 3 wt%). For concrete samples without TiO₂ (0, and 0,S) a similar RB color change is observed, albeit weak and not visible by direct inspection of figure 3. We tentatively attribute this to the presence of small amounts of photo-active oxide particles in concrete.

Assuming pseudo first-order photocatalytic reaction kinetics of Rz, the average reaction rates for reduction of Rz (blue to pink) obtained over several spots on the concrete sample are determined from RGB color change analysis to be approximately 7⋅10⁻³ min⁻¹ for both the pure and surface functionalized concrete (without addition of TiO₂ nanoparticles), thus indicating a weak photocatalytic activity. We attribute to small concentrations of photoactive oxide components in concrete. For the concrete samples with additions of TiO₂ nanoparticles the rate is not improved at low concentration of TiO₂ (1 wt%), and after surface functionalization it is even lowered (~ 6⋅10⁻³ min⁻¹). At higher TiO₂ concentrations (3 wt% and 5 wt%) the reaction rate increases by 40-60%, which is also manifested in the more distinct color changes (blue to pink) occurring over several parts of the concrete surfaces seen in figure 3.
Figure 4. Normalized red (R) and blue (B) color signals as a function of UV-A irradiation time extracted from the images depicted in figure 3. The hollow blue and red symbols (□ and ○) correspond to B and R values of pure concrete samples without addition of TiO₂, and solid symbols (■ and ●) the corresponding values for surface functionalized concrete samples containing varying amounts of TiO₂ as indicated in each diagram.

3.2 Wetting measurements
Figure 5 shows results from contact angle measurements on concrete, surface functionalized concrete, concrete with 5 wt% TiO₂, and surface functionalized concrete with 5 wt% TiO₂, respectively. The contact angle for all samples lies between ~10° to 15°, which is characteristic for hydrophilic surfaces, and it is slightly larger for the functionalized samples.

The latter result can be understood from the fact that chemical interactions are mostly dominated by the interfacial acid interactions which influence the strength of the adhesive bonds at the interface and thus control the wetting [13]. The increasing wetting angle on the chemically modified cement surface indicates exchange of protons between neighboring molecules and functional hydroxyl and sulfate groups [7].

Figure 6 shows top view photographs from sessile drop contact angle measurements on concrete samples (a) with 5 wt% TiO₂, and (b) surface functionalized concrete with 5 wt% TiO₂ corresponding to figure 5c and figure 5d, respectively.
Figure 5. Sessile drop contact angle measurements on (a) concrete, (b) surface functionalized concrete, (c) concrete with 5 wt% TiO₂, and (d) surface functionalized concrete with 5 wt% TiO₂.

In figure 6a it is seen that the water droplet is quickly spread on the sample without surface functionalization after it is applied on the surface, and that it absorbs in the hygroscopic concrete sample over a large surface area. In contrast, on the surface functionalized concrete sample shown in figure 6b, the wetting area is much smaller and stays as a drop on top of the surface for extend times, as water is repelled from the surface and slowly dries (evaporates).

Figure 6. Top view image from sessile drop contact angle measurements on concrete samples (a) with 5 wt% TiO₂, and (b) surface functionalized concrete with 5 wt% TiO₂.

Figure 7 shows results from rinsing test applied to concrete samples containing 5 wt% TiO₂ with and without surface functionalization. Droplets of 20 μl in volume were applied onto the sample surfaces, which were held at an angle of 45°, and the rinsing behavior was noticed as the drop flowed down the surface. It is evident that the droplet flows much more easily on the surface functionalized sample, and that much more water is absorbed on the non-functionalized sample leaving dark moisture
traces. This further shows that the surface functionalization repels water and improves the self-cleaning properties of the concrete surface.

Figure 7. Top view image from sessile drop contact angle measurements on concrete samples (a) with 5 wt% TiO$_2$, and (b) surface functionalized concrete with 5 wt% TiO$_2$. The tilting angle of the samples was 45° and the volume of the applied droplet was 20 μl. Water absorbs in the hygroscopic concrete sample without surface functionalization as it slides along its surface. On the surface functionalized concrete sample most water slides off and the trace of absorbed water is much smaller.

The modification of surface acidity can be utilized also to alleviate problems of deactivation in gas-phase photocatalysis. It is well-known that adsorption of reaction products inhibits adsorption of gas pollutants due to strong interaction with surface sites. In particular, carboxylic acids and their ions bind strongly to oxide surfaces such as TiO$_2$ [6]. This is due to formation of strongly bonded bridging bidentate carboxylate ions. The bonding of formate, which is a common intermediate in degradation of VOCs, is weakened on sulfated TiO$_2$ and results in considerable improvement of the sustained activity if the surface functionalized photocatalyst compared to untreated anatase TiO$_2$ [14].

4. Conclusions
We have shown that by mixing TiO$_2$ nanoparticles with reactive powder concrete and further chemically functionalize the casted concrete sample a surface with enhanced self-cleaning properties is obtained. In particular, the photocatalytic activity and the wetting properties of concrete samples made by mixing TiO$_2$ nanoparticles (0, 1, 3 and 5 wt% TiO$_2$) and reactive powder concrete have been measured with and without surface chemical functionalization. Samples containing 1-5 wt% TiO$_2$, regardless of surface functionalization, show enhanced activity. The surface functionalized concrete samples with 5 wt% TiO$_2$ concentration showed similar or even higher photocatalytic activity compared to the non-functionalized samples containing the same TiO$_2$ concentration. All samples – with and without surface functionalization – exhibited hydrophilic wetting properties. The self-cleaning properties as measured by the rinsing properties of applied water droplets at inclined sample angles were found to be superior for surface functionalized samples with added TiO$_2$. Water was found to slide off the surface of functionalized concrete samples without being absorbed in the hygroscopic, porous concrete surface much more readily than the non-functionalized sample containing the same TiO$_2$ concentration. We envisage that by adding thin TiO$_2$ layers on special concrete products, e.g. by spray pyrolysis, or otherwise, a protective and fully functional self-cleaning coating with added surface chemical properties can be obtained following the methods outlined here.
We have previously shown that sulphate surface functionalization of TiO$_2$ thin film glass leads to dramatically improved oleophobic properties [8, 9], and sustained gas-phase VOC photodegradation activity [14]. It should thus be straightforward to extend the surface functionalization scheme to other surfaces, such as tiles, metal sheets, and plastics. This development would open up possibilities to introduce a second generation of photocatalytic materials in the indoor setting with improved wetting properties combined with photocatalytic activity.

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