

# Roll-to-roll application of photocatalytic TiO<sub>2</sub> nanoparticles for printed functionality

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## ABSTRACT

In this work ultraviolet A (UVA) light controlled photocatalytic activity of TiO<sub>2</sub> nanoparticles is utilized on paper, paperboard, and plastic films for controlled wetting and oxygen sensors for modified atmosphere packages (MAPs). A liquid flame spray (LFS) process is used for a large-area TiO<sub>2</sub> nanoparticle deposition on natural fibre based substrates such as paperboard that results in a superhydrophobic surface. Controlled wettability is achieved using an UVA light activation that converts the surface to hydrophilic whereas an oven heat treatment recovers the initial superhydrophobicity. On the other hand, a TiO<sub>2</sub> nanoparticles with methylene blue (MB) dye is used to detect the presence of oxygen in modified atmosphere packages. We believe that photocatalytically active surfaces with tailorable properties will find many applications in the near future, for example, with printed functional devices.

**Keywords:** TiO<sub>2</sub>, nanoparticles, photocatalysis, controlled wetting, O<sub>2</sub> sensor

## 1 INTRODUCTION

Paper manufacturing has been known for almost two millennia since the initial discovery back to AD 105 when Ts'ai Lun reported the invention to the Emperor of China, and cellulose is the most abundant biopolymer on Earth with annual production up to  $1.8 \times 10^{12}$  tonnes [1]. The benefits of natural fibre based substrates such as paper, paperboard, micro- and nanofibrillated cellulose (MFC/NFC), and cellulose nanocrystals (CNC) include recyclability, renewability, biodegradability, and such sustainable substrates can be produced at a large scale cost-effectively. In recent years the decrease in the graphical art paper grades has shifted the focus of the research and development towards value-added products such as printed electronics and printed functionality on natural fibre based substrates.

Recently paper has found an increasing number of functional applications such as point-of-care (POC) diagnostics. Porosity of paper is then an advantage as the capillary pressure can be utilized for liquid actuation *e.g.* in

microfluidic paper-based analytical devices ( $\mu$ PADs) [2] or micropatterned paper [3] for colorimetric detection.

In this work we present ultraviolet A (UVA) light controlled photocatalytic activity of roll-to-roll (R2R) deposited TiO<sub>2</sub> nanoparticles on paper, board, and plastic films both for controlled wetting and oxygen sensors for modified atmosphere packages (MAPs). It is well-known [4] that a semiconductor TiO<sub>2</sub> is photocatalytically active with anatase crystalline form having bandgap energy of 3.2 eV corresponding to a photon wavelength of 388 nm. Such photocatalytically active TiO<sub>2</sub> nanoparticles and thin films have received much attention due to numerous industrial applications ranging from self-cleaning and antibacterial to anti-reflecting and anti-fogging properties [5-6].

We use here a liquid flame spray (LFS) process for large-area, R2R TiO<sub>2</sub> nanoparticle deposition on natural fibre based substrates. LFS is a versatile process suitable for formation of various metal and metal oxide nanoparticles that can be deposited on different substrates such as glass and paper in normal atmospheric conditions. In LFS process a liquid organometallic precursor dissolved in water or alcohol is fed into a high temperature and velocity flame in which the precursor evaporates and nucleates forming nanoparticles. The formed nanoparticle diameter can be controlled from 2 to 200 nm via the process parameters. An additional benefit of the LFS process is that the generated nanoparticles can be collected on a moving web, which allows large areas to be coated via roll-to-roll process flow [7].

We also demonstrate here an oxygen indicator based on a methylene blue (MB) indicator ink used with TiO<sub>2</sub> nanoparticles. Colorimetric oxygen sensors are based on reversible redox reaction of a dye that results in a change in the light absorption, and thus color. For example, MB has a clear change in color from blue in its oxidized state to transparent upon reduction. Therefore, such colorimetry-based inks can be used to improve food safety and to reduce the amount of wasted food by introducing cost-effective oxygen sensors into modified atmospheric packages (MAPs). MAPs are nowadays extensively used to extend the shelf life of fresh food products such as meat, fish, coffee, bread products, fruit and vegetables.

Development of the MAPs has resulted in major improvements in the storage, distribution, and logistics in

the supply chain. Atmospheric oxygen induces oxidation of *e.g.* fats and oils, and fresh meat turns from red to brown as the pigments interact with oxygen. Secondly, food spoiling bacteria such as *Escherichia coli* are more easily grown in atmospheric conditions although they can survive in anaerobic conditions as well. Therefore, better tissue preservation is obtained using the MAPs as physiological processes and bacterial growth can be slowed down [8]. The most typically used gases in the MAPs are O<sub>2</sub>, N<sub>2</sub> and CO<sub>2</sub> depending on the application: for example, pork requires anaerobic conditions whereas a mixture of O<sub>2</sub> and CO<sub>2</sub> is used for beef.

There is still a need for improvement of the MAPs although commercial oxygen indicators are already available in the market. The cost of these solutions is significantly higher (unit cost in the range of 0.20 to 1.0 USD) than the case presented here (unit cost less than 0.01 USD). At the moment, the commercially available sensors are more expensive than the package itself. Secondly, anaerobic storage and handling is also often required that hinders their use in industrial applications.

Food safety can be improved and the amount of waste food can be reduced by introducing cost-effective oxygen sensors into MAPs. Furthermore, under right storage conditions it may also be possible to extend the shelf life of the packed products. In this work the presented sensor based on MB/TiO<sub>2</sub> mixture enables a long storage time in air and utilizes a simple UV activation process. We believe that our results can be used for a significant cost reduction in manufacturing and thus widen the application potential of oxygen indicators in MAPs.

## 2 EXPERIMENTAL

### 2.1 Liquid flame spray

The wetting properties of commercially available double pigment coated paperboard (grammage 200 g/m<sup>2</sup>, Natura, Stora Enso, Skoghall, Sweden) were altered by the deposition of TiO<sub>2</sub> nanoparticles. The liquid flame spray (LFS) process was used with a liquid precursor of titanium (IV) isopropoxide (TTIP) that was dissolved in isopropanol (IPA) for the deposition of TiO<sub>2</sub> nanoparticle coating on paperboard. Metal ion concentration of 50.0 mg/ml was fed with a rate of 32.0 ml/min into a nozzle that was fixed at 15 cm distance from the substrate.

The TiO<sub>2</sub> nanoparticle coated surface was exposed to UVA light (Bluepoint 4 ecocure, Hönle UV Technology, Germany) at a central wave-length of 365 nm, with a 320–390 nm filter. Irradiation at a constant intensity of 50 mW/cm<sup>2</sup> for 30 min induced a change in the surface properties from superhydrophobic to hydrophilic. To recover the initial hydrophobicity, the samples were placed in an oven at 150°C for 3 min.

Chemical composition of the substrate surfaces after the LFS treatment were studied by using a water contact angle goniometer (KSV CAM 200, KSV Instruments Ltd., Finland). Surface images were acquired using a field-

emission FESEM in secondary electron mode (LEO Gemini 1530 with in-lens detector, Zeiss, Germany). The acceleration voltage and working distance were 5 kV and 5 mm. The magnification used was 10 000×. Furthermore, X-ray photoelectron spectroscopy (XPS) (PHI Quantum 2000, Physical electronics instruments, USA) equipped with a monochromatic Al K  $\alpha$  X-ray source and operated at 25W, where the charge compensation was enhanced by combination of electron flood and ion bombarding were utilized.

### 2.2 Methylene blue - TiO<sub>2</sub> indicator ink

The indicator ink was made by blending methylene blue (Sigma Aldrich), TiO<sub>2</sub> nanoparticles (E171) (Sigma Aldrich) and glycerol (GC, Sigma Aldrich) in ethanol or water using a magnetic stirrer. MB is most soluble in water, but the solubility in ethanol was adequate to prepare a suitable ink for printing without using additional ion-pairing with dodecyl sulfate. Solubility can also be increased by, for example, adding urea to the ink formulation, but this resulted in a slower and thus poorer UV-activation. With water based inks a surfactant was added for wetting on plastic substrates. An ink based on 2 wt. % MB:TiO<sub>2</sub>:GC (1:6:2) in ethanol was used in reverse gravure coating. For flexographic printing, the viscosity was increased by increasing the solid concentration to around 5 wt.% of MB:TiO<sub>2</sub>:GC (1:10:4) in ethanol with ethylene glycol (Sigma Aldrich). Flexographic ink was printed both on paper and plastic substrates. The barrier curtain coated paper contains a commercial finepaper (Lumipress 115, StoraEnso, FI) as basepaper with a 10 g/m<sup>2</sup> barrier layer consisting of platy kaolin (Barrisurf HX, Imerys Minerals Ltd, UK) blended with 50 pph ethylene acrylic latex (Aquaseal 2077, Paramelt B.V., NL). The paper was twice calendered through a soft nip with a line load of 120 kN/m and a temperature of 25°C. Plastic reference substrate was commercially available poly(ethylene phthalate) (PET) film (Mylar®A, Dupont). All components of the developed oxygen indicator are nontoxic.

Reverse mode gravure coating was performed on a MiniLabo test coater (Yasui Seiki Co., USA) using a trihelical gravure roll with 80 lines/inch (31.5 lines/cm) and a diameter of 2 cm at a web speed of 1.0-1.6 m/min and a roll speed of 30 rpm *i.e.* a roll surface speed of 1.9 m/min. Flexographic printing was carried out using a custom-built R2R mini pilot scale printer with a web width of 10-12cm with commercial ASAHI DSH® (Shore A 69°) photopolymer plates located at the Abo Akademi University, Finland. The used ceramic anilox cylinder (Cheshire Engraving Services Ltd., UK) had a cell angle of 60° with 118.7 lines/cm and a cell volume of 17.2 cm<sup>3</sup>/m<sup>2</sup>. The printing speed was 10m/min and two 500W infrared drying units (HQE 500, Ceramicx, IRL) (700°C) were mounted 15 cm after the printing nip with a distance to substrate of 3 cm.

### 3 RESULTS

We have studied both surface topographical and chemical composition of nanoparticle coated paperboard to explain observed differences in surface wettability. Figure 1 displays the SEM image of TiO<sub>2</sub> nanoparticle coated surfaces. From the image we observe that the paperboard surface is fully covered by the nanoparticles, which form a complex coating structure containing a number of summits and voids. The sizes of nanoparticles range between 40-80 nm, as shown by SEM and AFM images reported in our previous work [9].

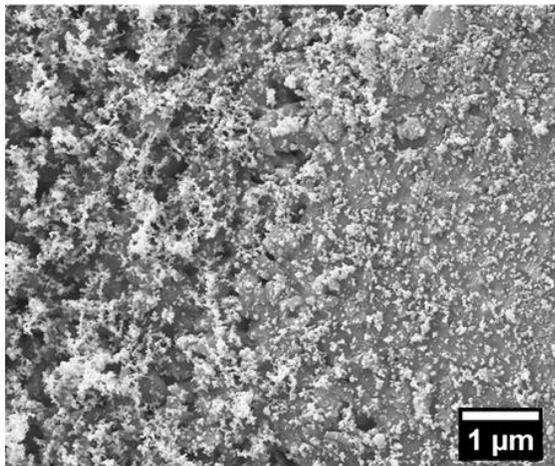


Figure 1: FESEM image of the LFS TiO<sub>2</sub> nanoparticle coated paperboard.

Figure 2 shows the water contact angle (CA) values for TiO<sub>2</sub> coated sample before UVA irradiation, and after cyclic alternations of 30 min UVA exposure and 3 min oven treatments. It was observed that superhydrophobic TiO<sub>2</sub> surfaces with water CA of 161° are changed to hydrophilic with water CA of 6° by the UVA light. Full hydrophobicity recovery is achieved by placing the sample into oven for 3 min.

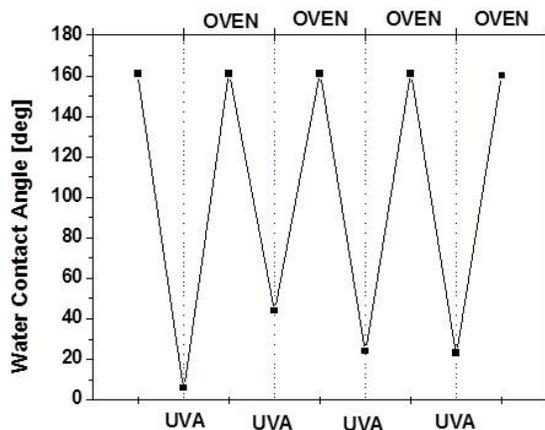


Figure 2: Wettability conversion of TiO<sub>2</sub> nanoparticle coated paperboard with UVA illumination and oven heat treatment.

The changes in the wettability correlate well with the changes observed in the surface chemistry using an X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) [10]. However, the achieved wettability conversion is reversible *i.e.* the recovery of surface hydrophobicity occurs under ambient conditions in dark during storage, and the change can be accelerated by a heat treatment.

Figure 3 shows a reverse gravure coated thin film of MB/TiO<sub>2</sub> indicator ink on a plastic film. We have used UVA light activation with a photomask to generate patterned oxygen indicator films such as 1D and 2D barcodes, and examples of such patterned sensors are shown in Fig. 3 that prevent misinterpretation by unwanted photobleaching during the package storage.

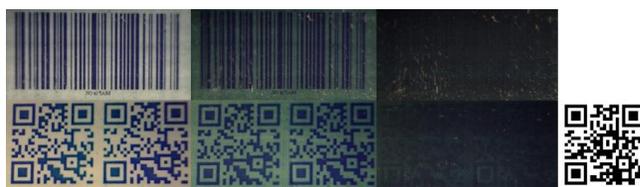


Figure 3: UV patterned 1D and 2D (QR) barcodes are shown after the UV exposure and after subsequent exposure to air for 30 min and 2 h, respectively.

There are three possible interpretations of the oxygen indicator. First, no oxygen leak has taken place if the pattern is clearly visible. Secondly, there has been an oxygen leak if the whole indicator pattern is faded away to blue *i.e.* to oxidised MB. Finally, the indicator has unintentionally been exposed to UV light during the storage if the whole pattern fades away to white, and the indicator cannot be trusted anymore. An additional advantage with the patterning approach is that a high image resolution of oxygen indicator films can be achieved with relative ease. It is also simple to change the pattern or figure even if the films are printed inside the lid of the MAP. Furthermore, an additional advantage is that there is no need for a white background behind the pattern due to the large contrast between the white UV exposed part of the pattern and the unexposed blue areas.

The most straightforward way of producing patterned colorimetric indicators at very low cost and high throughput is to use a conventional flexography printing. Examples of flexography printed oxygen indicator patterns were done both on paper and plastic film. Paper has several advantages over the plastic film: it is made from renewable materials, recyclable, less expensive, and has a reflective natural white background having a good contrast compared to the limited contrast of the printed patterns on plastic film on a dark background. In addition, the print resolution and adhesion of the ink onto paper was much better than on plastic film. A minor squeeze effect was observed on plastic film. On the other hand, paper has no squeeze as there is better adhesion and absorption into the porous paper substrate.

Paper porosity needs to be well-controlled: with an absorptive paper substrate with poor barrier properties the indicator performance was poor, and it was not even possible to activate with UV-light within a reasonable time or without irreversible photobleaching.

In high porosity papers the MB dye is absorbed into the paper substrate and consequently, the dye is no longer in contact with the TiO<sub>2</sub> nanoparticles on the surface. The oxygen indicator can be operated by using a paper substrate with sufficient barrier properties and by increasing the amount of TiO<sub>2</sub> in the indicator ink. Nevertheless, higher UV exposure times were still required for photobleaching the pattern on paper than on plastic film and the response to oxygen was also slower on the paper substrate. Figure 4 shows the result of flexographic printed oxygen indicator on plastic film on top of white background. The presence of oxygen is clearly seen as the transparent ink is converted to oxidized bright blue color.



Figure 4: Flexographic printed oxygen indicator on plastic film before and after 30 s UV exposure, and after exposure to air for 10 min and 2.5 h, respectively.

## 4 CONCLUSIONS

As a conclusion we have studied the photocatalytic activity of TiO<sub>2</sub> nanoparticles for controlled wettability of nanoparticle coated paperboard and for colorimetric oxygen indicators in the modified atmosphere packages.

Controlled wettability is achieved using an UVA light activation that converts the surface to hydrophilic whereas an oven heat treatment recovers the initial superhydrophobicity. Such surfaces with controlled wettability are expected to find applications, for example, in microfluidic point-of-care type diagnostic devices.

There is also an increasing demand in market for cost-efficient oxygen indicators as the use of MAPs increases. At the same time consumers request more information about the safety and quality of the food. We have demonstrated here that it is possible either coat or print in a roll-to-roll process flow UV activated colorimetric oxygen indicators with a very low unit cost both on paper and plastic film. The developed sensors are nontoxic, robust and easy to handle in atmospheric conditions. The maximum contrast between the exposed to unexposed areas was 80 % reflectivity to 1 % after air exposure. Moreover, the response time can easily be controlled by varying the process parameters such as the UV exposure time and intensity, polymer binder or MB/TiO<sub>2</sub> ratio as well as printing or coating barrier layers. We have also presented

patterned structures that avoid the problem of unintentional exposure to the UV light. This further enhances the safety aspects of the developed oxygen indicators. The influence of MB / glycerol penetration into the porous paper coating structure will be studied in a future communication. Furthermore, the required UV intensity for the label activation and the shelf life of the printed sensors will also be investigated in further detail. Finally, the developed indicators have a large commercial potential as they can cost-effectively be integrated into the manufacturing line.

We believe that photocatalytically active surfaces with tailorable properties will find many applications in the near future such as controlled wetting surfaces or with printed functional devices *e.g.* roll-to-roll printed oxygen indicators for safe and smart packaging.

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