

Innovative semi-transparent nanocomposite films presenting photo-switchable behavior and leading to a reduction of the risk of infection under sunlight

Cite this: *RSC Advances*, 2013, 3, 16345

Received 5th June 2013,

Accepted 16th July 2013

DOI: 10.1039/c3ra42762e

www.rsc.org/advancesS. Rtimi,^a C. Pulgarin,^{*a} R. Sanjines^b and J. Kiwi^{*c}

Novel sputtered polyethylene–TiO₂ (PE–TiO₂) thin films induce fast bacterial inactivation with concomitant photo-switchable hydrophobic to hydrophilic transition under light. RF-plasma pretreatments allowed an increased TiO₂ loading on PE, favorably affecting the photocatalyst performance. ATR-FTIR spectroscopy shows that the increase in the cell lipid-layer fluidity leads to cell wall scission/bacterial inactivation.

The stable, strong adhesion of TiO₂ films to glass, iron plates, textile fabrics and thin polymer films active under solar light irradiation is a subject of timely research involving TiO₂ self-cleaning and inactivation properties.^{1–4} Several methods are used to prepare TiO₂ thin films, based on sol–gel processing depending on the heat resistant of the selected substrate. Sol–gel processing is the most commercially commonly used method to prepare TiO₂ films⁵ but the thickness of the TiO₂ films is not reproducible, they are not mechanically stable, and they exhibit low adhesion since they can be wiped off by a cloth or thumb.^{6–8} Polyethylene (PE) is a low cost, inert and mechanically strong thin flexible polymer. For this reason PE has been selected as the support for the semi-transparent TiO₂ films we report in this study.

The low surface energy of PE leads to poor particle adhesion. For this reason the PE was pretreated by RF and UVC to produce highly functional self-cleaning and anti-bacterial coatings increasing the surface sites able to bind TiO₂ nanoparticles.⁷ The plasma pretreatment has been reported to increase the polymer polarity, roughness and hydrophilicity, improving its binding capacity and interfacial adhesion.^{2,6} RF-plasma pretreatment of surfaces enhancing the antibacterial activity has been reported.^{3–5} The RF-plasma pretreatment of PE induces negatively charged functional groups, e.g., carboxylic, percarboxylic, epoxide and peroxide groups by the atomic O, excited O, anionic and cationic O in the

gas in the RF chamber. These O-species interact with the functionalized –CH₂–CH₂– groups of PE binding TiO₂ by electrostatic attraction. Reports by: Sarakinos, *et al.*,⁹ Kelly *et al.*,¹⁰ Parkin *et al.*,¹¹ Foster *et al.*,¹² Yates, *et al.*,¹³ report the sputtering and CVD deposition of TiO₂ on different surfaces.

The objectives of this study are: a) to present RF-plasma pretreated TiO₂–PE sputtered uniform adherent films showing fast bacterial inactivation kinetics, b) to show light induced hydrophobic to hydrophilic reversible switchable behavior in PE–TiO₂ films and c) to show by ATR-FTIR that the increase in the cell lipid layer fluidity during the loss of cell viability leads to bacterial cell-wall scission.

The low density polyethylene (LDPE) consists of highly branched low crystalline semi-transparent film with the formula H(CH₂–CH₂)_nH. The PE was pretreated in the cavity of the RF-plasma unit (Harrick Corp. 13.56 MHz, 100 W).^{3,8} The details of both pretreatment methods on C-rich surfaces have been recently described.^{3–5} The TiO₂ was sputtered by direct current magnetron sputtering (DC) on polyethylene as reported out of our laboratory.^{4,8} Before sputtering the films, the residual pressure P_r in the sputtering chamber was set to $P_r \leq 10^{-4}$ Pa. The substrate target distance was set at 10 cm. The TiO₂ thin films were deposited by reactive DC-magnetron sputtering (DC) in an O₂ gas flow from a 5 cm diameter Ti-target 99.99% pure (Kurt J. Lesker, East Sussex, UK). The current on the Ti target was set at 280 mA, at a power of 128 Watt (–518 V). The samples of *Escherichia coli* (*E. coli* K12) were obtained from the Deutsche Sammlung von Mikroorganismen und Zellkulturen GmbH (DSMZ) ATCC23716, Braunschweig, Germany, to test the antibacterial activity of the PE–TiO₂ sputtered fabrics, and details of the evaluation of *E. coli* during the inactivation process have been recently reported.^{5,8} The photo-induced super-hydrophilic hydrophobic transformation was evaluated on the PE–TiO₂ surface by the sessile drop method on a DataPhysics OCA 35 unit. The ATR-FTIR spectra were measured in a Portmann Instruments AG spectrophotometer equipped with a Specac attachment (45° one pass diamond crystal). The position of the IR peaks was found by the second derivative of the spectra after Fourier deconvolution. The effective mass of the TiO₂ used in the different samples was determined by X-ray fluorescence (XRF)

^aEcole Polytechnique Fédérale de Lausanne, EPFL-SB-ISIC-GPAO, Station 6, CH-1015, Lausanne, Switzerland. E-mail: cesar.pulgarin@epfl.ch; Fax: +41 (0)21 693 56 90; Tel: +41 (0)21 693 47 20

^bEcole Polytechnique Fédérale de Lausanne, EPFL-SB-IPMC-LNNME, Bat PH, Station 3, CH-1015, Lausanne, Switzerland

^cEcole Polytechnique Fédérale de Lausanne, EPFL-SB-ISIC-LPI, Bat Chimie, Station 6, CH1015, Lausanne, Switzerland. E-mail: john.kiwi@epfl.ch

Table 1 X-ray fluorescence determination (XRF) analyses of TiO₂ on PE samples sputtered for 8 min with and without PE-pretreatment

Pretreatment type and time	Surface TiO ₂ wt%/wt PE
PE-TiO ₂ , no pretreatment	0.0511
PE-TiO ₂ , RF plasma pretreated under vacuum 15 min (1 torr)	0.0815
PE-TiO ₂ , RF air plasma pretreated for 15 min	0.0959

in a PANalytical PW2400 spectrometer. Table 1 shows the results for the PE-TiO₂ samples sputtered for 8 min with and without RF-pretreatment.

Fig. 1a shows the *E. coli* inactivation on PE-TiO₂ films under simulated solar light for non-pretreated TiO₂ samples sputtered for different times. The sputtering time of 8 min shown in Fig. 5, trace (1) led to the most effective TiO₂ loading of PE and this trace was subjected to statistical analysis. PE-TiO₂ samples sputtered for 1–5 min did not deposit sufficient TiO₂ to drive the bacterial inactivation. Samples sputtered for 10 min, Fig. 1a, trace (2), led to a layer thickness >45 nm. This latter thickness increases the bulk inward diffusion of the photo-induced TiO₂ charge carriers responsible for the charge transfer between the PE-TiO₂ and bacteria.¹⁴ The light dose of the solar simulator used was tuned to 50 mW cm⁻², for the runs reported in Fig. 1–3.

Fig. 1b, trace (1) shows the fastest bacterial inactivation, within 60 min for PE-TiO₂ films previously RF-pretreated in air for 15 min and then sputtered for 8 min. RF-pretreatment for 5 min (Fig. 1b, trace 4) did not induce enough oxygenated functional groups on the PE surface to bond a high amount of TiO₂ mediating *E. coli* inactivation. Fig. 1b, traces 2 and 3 show that samples RF-pretreated for 20 and 30 min respectively did not lead

to faster bacterial inactivation kinetics compared to samples RF-pretreated only for 15 min. RF-plasma at 100 W induced a local heating in the PE, breaking intermolecular bonds (H-bonds) and partially segmenting PE with temperatures >160 °C produced during nano- or microseconds and not introducing permanent damage into the PE surface.^{4,6,8}

The optical absorption for samples pretreated by RF-plasma and sputtered for 1–3 min lead to transparent PE-TiO₂ films. These films show no significant absorbance and very low antibacterial activity. A decrease of ~5% or more in optical transmittance has been reported for RF-plasma pretreated PE due to the inherent high refractive index of TiO₂.¹⁵ Fig. 2 illustrates the rate of photo-induced hydrophilicity and the restoration of the hydrophobicity in the dark as a function of “cos θ”. According to Young’s theory,^{2,14} the “cos θ” of a liquid droplet on a solid surface is a function of the interfacial energy between the solid and liquid. That bacterial inactivation in the dark did not lead to bacterial inactivation suggests that the hydrophobicity of the non-irradiated PE-TiO₂ films remained stable.

The rate of the hydrophobic to hydrophilic conversion and of the reverse reaction in Fig. 2a and 2b were 2.77 × 10⁻¹ min⁻¹ and 8.71 × 10⁻³ min⁻¹ respectively. These rates were calculated by integrating “cos θ” in the Young’s eq. $\cos \theta = c\gamma^{1/2} - 1$, where γ is the surface free energy and $t = \infty$ corresponds to interfacial energy of the hydrophobic surface before irradiation. This surface energy increases upon illumination since the TiO₂ surface is transformed into a metastable hydrophilic state decreasing the initial contact angle in Fig. 2a from 121° to <5° after 60 min illumination. The reversible reaction back to the initial state within 24 h was monitored in Fig. 2b, showing the contact angle increase from 37° up to ~118°.

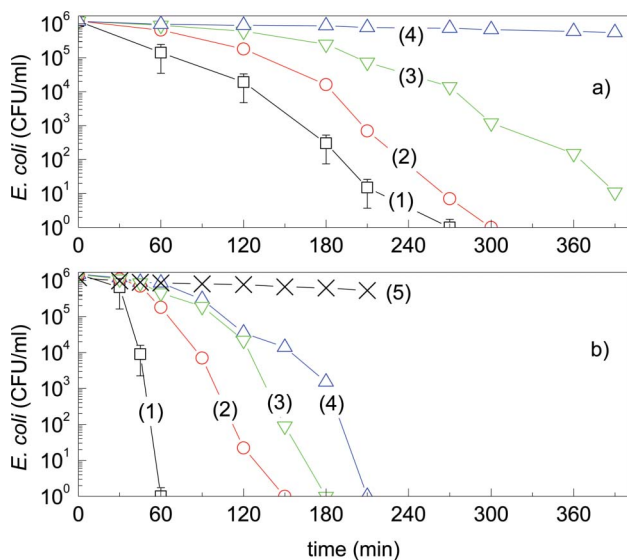


Fig. 1 *E. coli* inactivation on TiO₂ sputtered on PE for 8 min irradiated with simulated solar light. a) TiO₂ sputtered for different times without RF-plasma pretreatment for: (1) 8 min, (2) 10 min, (3) 5 min and (4) polyethylene alone, b) TiO₂ sputtered for 8 min after RF air plasma pretreatment for: (1) 15 min, (2) 20 min, (3) 30 min, (4) 5 min and (5) PE alone RF air pretreated for 15 min.

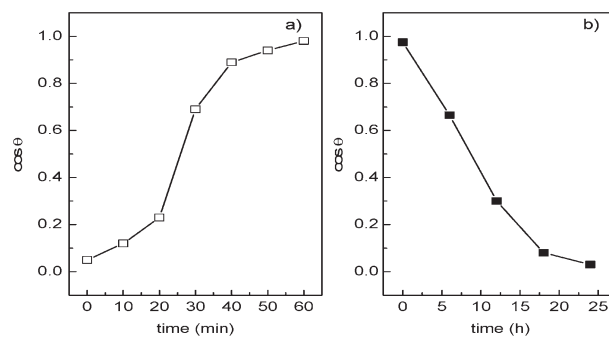


Fig. 2 a) cos θ plot of the switchable induced transition of PE-TiO₂ (sputtered for 8 min and RF plasma pretreated for 15 min) kinetics under solar simulated irradiation and b) dark reverse reaction kinetics towards the initial state.

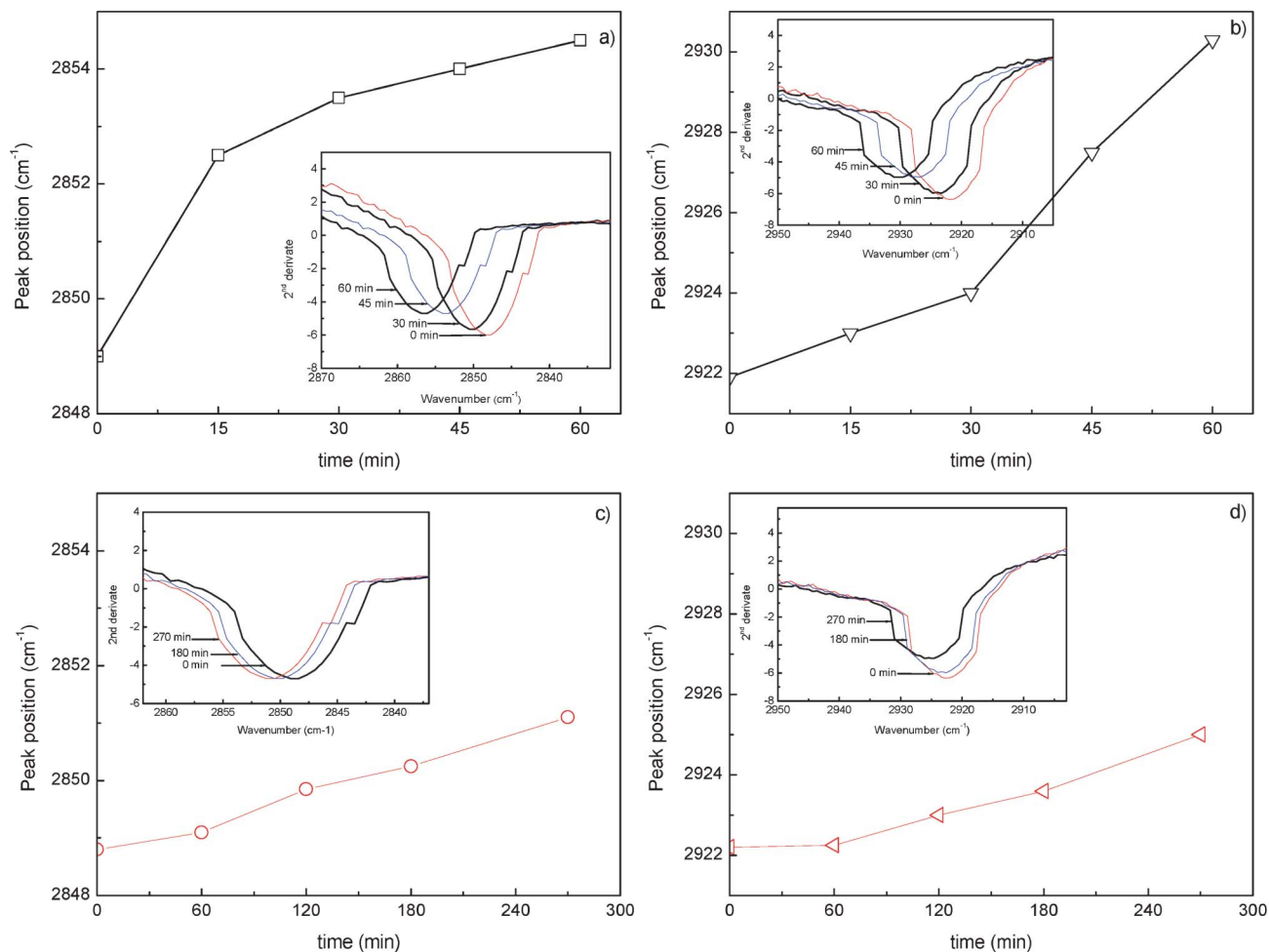
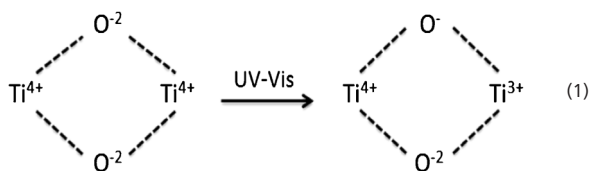


Fig. 3 Change in the second derivative of the ATR-FTIR peaks for the asymmetric $\nu_a(\text{CH}_2)$ vibrational bands and the symmetric $\nu_s(\text{CH}_2)$ vibrational bands up to 60 min under solar simulated irradiation for *E. coli* under light. Fig. 3a and 3b show the IR shifts for PE-TiO₂ samples pretreated with RF plasma for 15 min and sputtered for 8 min. Fig. 3c and 3d show the IR shifts for PE-TiO₂ samples without RF-plasma pretreatment sputtered for 8 min.



The hydrophobic to super-hydrophilic TiO₂ transition activated by UV-vis irradiation induces the metastable TiO₂ hydrophilic species shown in eqn (1). The reuse of the PE-TiO₂ samples during several cycles led to a stable bacterial loss of viability. This means that the RF-plasma pretreatment anchored TiO₂ nanoparticles on PE, but did not destroy the PE network. Tennakone *et al.*,¹⁶ and Ohtani *et al.*,¹⁷ have shown that TiO₂ embedded on the PE surface by sol-gel methods induced PE-surface degradation, limiting its photocatalytic performance. Recently, R. Amal reported reversible photo-switching behavior under light by Ag-nanoparticles.¹⁸

The photocatalytic peroxidation of the *E. coli* cell wall membrane gives rise to the shift reported in Fig. 3. Fig. 3a shows the shift of the asymmetric methylene peak at $\nu_a(\text{CH}_2)$ 2922.2 cm⁻¹ and of the symmetric $\nu_s(\text{CH}_2)$ 2849.2 cm⁻¹ peak of the cell-

wall under light irradiation up to 60 min. The shift was recorded on the sample RF-plasma pretreated for 15 min, and sputtered for 8 min. This shift is important since the (CH₂)- and (CH₃)- groups make up 70% of the cell wall content in the three *E. coli* cell-wall envelopes. The progressive decrease of the asymmetric ν_a and ν_s symmetric bands is shown in the insert to Fig. 3a and 3b. As the irradiation progresses, the shift of the asymmetric $\nu_a(\text{CH}_2)$ and the symmetric $\nu_s(\text{CH}_2)$ peaks reflects larger intermolecular C-H bond distances.¹⁹ The IR shifts for sputtered PE-TiO₂ films RF-plasma pretreated in Fig. 3a and 3b are seen to be more significant compared to the non-pretreated samples shown in Fig. 3c and 3d under the same experimental conditions. This fact is due to the lower amount of TiO₂ on the non RF-pretreated PE leading longer bacteria inactivation times. The shifts shown in Fig. 3 have been assigned to an increase in the cell-wall fluidity during the *E. coli* photocatalyzed inactivation by way of TiO₂ dispersions.^{20,21} This suggests that increasing the lipid fluidity induces damage/permeabilization into the *E. coli* cell wall functional groups.

Conclusions

By sputtering methods, uniform and adhesive thin TiO₂ semi-transparent layers allowing considerable light transmittance were deposited on pretreated PE. These thin flexible films show antibacterial properties under light. TiO₂ sputtered, RF-plasma pretreated PE led to a fast bacterial loss of viability compared to non-pretreated PE. The reversible hydrophobic to hydrophilic kinetics conversion of PE-TiO₂ under simulated solar irradiation was followed by contact angle. The innovative PE-TiO₂ films described in this study may have high potential for practical applications.

Acknowledgements

We thank the Swiss National Science Foundation (SNF) for the financial support of the Project: Preparation, testing and characterization of innovative intravascular catheters inactivating bacteria by contact (oligodynamic effect) and the COST Actions MP1101, MP1106 and TD 0906 for interactive discussions during the course of this study.

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