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Solar photocatalytic disinfection using ink-jet printed composite TiO_2/SiO_2 thin films on flexible substrate: applicability to drinking and marine water

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Abstract

Hybrid TiO_2/SiO_2 thin films deposited by material printing technique on flexible substrates were prepared, characterized and tested for solar photocatalytic disinfection. Effect of surface hydrophilicity/hydrophobicity of printed coatings on photocatalytic disinfection was studied by means of i) drinking water contaminated with natural consortia of fecal bacteria (gram-negative: *Escherichia coli* and total coliforms; gram-positive: *Enterococci*), and ii) seawater containing pathogenic gram-negative bacteria (*Vibrio owensii, Vibrio alfacsensis and Vibrio harveyi*). Inactivation of gram-negative bacteria in drinking water with fecal contamination by solar photocatalysis was slightly more efficient than solar disinfection, while for gram-positive bacteria similar efficiency was observed. These results, in combination with observed release of titanium from coatings (detected by means of inductively coupled plasma atomic emission spectrometer), indicate that TiO_2/SiO_2 needs further improvements for solar photocatalytic disinfection of drinking water. Efficiency of seawater disinfection towards gram-negative *Vibrio* spp. (*Vibrio owensii, Vibrio alfacsensis and Vibrio harveyi*) was significantly enhanced when TiO_2/SiO_2 coatings were used under natural solar light. Moreover, hydrophobic thin films led to faster *Vibrio* spp. inactivation as compared to hydrophilic ones, which was attributed to higher bacteria adhesion on hydrophobic coatings. However, decrease of photocatalytic activity of hydrophobic TiO_2/SiO_2 coatings was observed after ten experimental

cycles mainly due to deposition of salts on the surface of photocatalyst. Generally, results of this study suggest that autochthonous bacteria such as *Vibrio* spp. in seawater are significantly more resistant to solar disinfection in comparison with not autochthonous bacteria such as *Escherichia coli*, total coliforms and *Enterococci* in contaminated drinking water.

Keywords: solar photocatalysis; flexible thin films; drinking water; marine water.

1. Introduction

One of the most applied methods for disinfection of drinking water and wastewater is chlorination. It benefits from high efficiency and low cost of the treatment. However, the main drawback of this disinfection method is the generation of potentially harmful disinfection byproducts (Singer et al., 1995). Alternative disinfection methods such as ozonation (Dong et al., 2018, Nasuhoglu et al., 2018), UV (Moreno-Andrés et al., 2016, Aguilar et al., 2018), advanced oxidation processes (AOPs) (Moreno-Andrés et al., 2016, Moreno-Andrés et al., 2018b, Moreno-Andrés et al., 2017a), etc. are widely studied. It should be mentioned that application of AOPs for water disinfection leads not only to inactivation of pathogenic microorganisms but also to decomposition of organic pollutants in water (Levchuk et al., 2018, Levchuk et al., 2015, Levchuk et al., 2016, Fernández-Ibáñez et al., 2015). Among different AOPs solar heterogeneous photocatalysis attracted extensive attention of researchers in recent years (Malato et al., 2016). Most studied photocatalytic material in heterogeneous photocatalysis is titanium dioxide (TiO_2). This photocatalyst is highly beneficial due to relatively high efficiency, low cost and chemical non-toxicity (Carp et al., 2004, Eufinger et a.,l 2008, Fujishima et al., 2000). However, TiO_2 is mostly used in slurry systems, which represents one of the main drawbacks for water treatment as separation of TiO_2 from water is costly operation (Bideau et al., 1995, Shan et al., 2010). Hence, immobilization of photocatalyst on support can be highly beneficial for application of photocatalysis for water disinfection, especially for treatment of small volumes of water in remote communities without proper water supply (Loeb et al., 2018) and as possible future water treatment method using renewable solar energy in industrialized countries. Commonly used hard substrates for photocatalytic coatings are glass (Bideau et al.,1995, Gelover et al., 2004, Serpone et al., 1986, Ryu et al., 2003, Mansilla et al., 2006, Lopez et al., 2013, Espino-Estévez et al., 2015), activated carbon (Gao et al., 2011, Xue et al., 2011), polymers (Fabiyi and Skelton, 2000, Tennakone et al., 1995, Damodar and Swaminathan, 2008), silica gel (Li et al., 2014, Zainudin et al., 2010, Negishi et al., 2012), metal foams (Levchuk et al., 2016,

Plantard et al., 2011, Plesch et al., 2009, Vargová et al., 2011, Guo et al., 2010, Santiago et al., 2015) etc. However, there is a rising interest in the preparation of photocatalytic coatings on flexible substrates, such as polyethylene terephthalate, polyester, polyurethane, etc. (Gregori et al., 2014). One of the main advantages of photocatalytic materials deposition on flexible substrates is the possibility to use coatings in almost any type of photoreactors due to its high level of flexibility. Several studies reported preparation of photocatalytic coatings on flexible substrates for various applications (Gregori et al., 2014, Homola et al., 2016, Yan et al., 2017, Vodišek et al., 2018, Xu et al., 2018, Zhao et al., 2017, Yan et al., 2016, Hatamie et al., 2015, Dzik et al., 2015). However, only few studies reported bacteria inactivation by photocatalytic coatings deposited on flexible substrates under simulated solar irradiation earlier (Baghriche et al., 2013, Rtimi et al., 2014, Rtimi et al., 2016). This can probably be attributed to challenges for application of flexible thin films for water disinfection such as relatively poor stability of the coatings, which may lead to release of the photocatalyst to the water (Levchuk et al., 2016).

The main goal of this work was to estimate the efficiency and stability of hydrophobic and hydrophilic photocatalytic coatings deposited on flexible substrate for different application in solar photocatalysis. In order to achieve this goal, hydrophobic and hydrophilic TiO_2/SiO_2 thin films were printed on flexible substrates. Feasibility of printed coatings was tested for two possible applications of solar photocatalysis. The first application was inactivation of natural consortia of fecal bacteria in drinking water, which is of high importance for the production of safe potable water in cases of natural disasters, for instance. The second studied application of solar photocatalysis was inactivation of pathogens in seawater, which is an interesting alternative to UV disinfection of aquaculture effluents.

2. Materials and Methods

2.1. Preparation of TiO_2/SiO_2 thin films on flexible substrate

Polyethylene terephthalate (PET) with a total thickness of 150 μm was used as a flexible substrate. The photocatalytic mesoporous TiO_2/SiO_2 film was deposited using an experimental Fujifilm Dimatix 2831 inkjet printer on samples with dimensions 25 × 12 cm^2. The ink was prepared by mixing 6 mL of TiO_2 dispersion (20 wt% of nanoparticulate titania Evonik P25 in Dowanol® PM (1-methoxypropan-2-ol) with 2 mL of a recently-reported organosilica binder (Gregori et al., 2014) (20 wt% in anhydrous ethanol) and 8 mL of isobutanol. Approx. 2 cm^3 of 1 mm glass balls were added to this in a 20 mL glass vial and

this was placed overnight on an oscillating shaker set to 1000 rpm. Thus, the TiO_2/SiO_2 ratio was 75:25 and the thickness of the coating was approx. 300 nm. The materials and procedures employed for the printable suspension formulation have been reported in detail in our previous work (Homola et al., 2016).

2.2. Characterization of printed coatings

A MIRA3 scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy EDX (Tescan, Czech Republic) was used to evaluate the morphology and chemical composition of TiO_2/SiO_2 thin films. Scanning electron microscope Nova NanoSEM 450 was used to study behavior of bacteria on the surface of coatings before and after photocatalytic tests.

The TiO_2/SiO_2 surfaces were further investigated by X-ray photoelectron spectroscopy (XPS) using an Al Kα ESCALAB 250Xi apparatus (Thermo Fisher Scientific). All samples were measured at 650 μm spots at a takeoff angle of 90° in 10^{-8} mbar vacuum at 20 °C. An electron flood-gun was used to compensate for charges on sample surfaces. The spectra were referenced to C 1s at 284.8 eV.

TiO_2/SiO_2 films characterized by SEM and EDX were deposited on Fluorine doped Tin Oxide (FTO) glass to avoid covering the TiO_2/SiO_2 with conductive layers, which might compromise the chemical composition of the surface measured by EDX. On the other hand, the use of FTO is also not ideal, because the penetration of EDX in case of mesoporous and porous films might be higher than the thickness of the coating. TiO_2/SiO_2 films, characterized by XPS, were deposited on cleaned glass slides instead of PET. This was to avoid detecting any strong ″parasitic″ carbon signal from PET substrate which might mix with carbon content measured on the surface of TiO_2/SiO_2. The value of carbon content is a crucial indicator of the efficiency of plasma treatment.

The water contact angle on the surface of hydrophobic and hydrophilic coatings was measured by means of OCA 15plus (NEURTEK Instruments) connected to the digital camera. The droplets of Milli-Q water with volume of 5 μL were deposited on different places on the surface of the coatings before photocatalytic tests and recorded. Mean values were estimated from three measurements.

The water uptake study was performed on samples with the dimension of 2 × 1 cm^2 attached to a digital weight to measure the force. The force was measured for 40 s and the sample was brought into contact with the water surface at time 5 s.

Plasma treatment

The atmospheric-pressure ambient air plasma (RPS400 for roll-to-roll, Roplass s.r.o., Czech Republic) was employed to modify the surface of TiO_2/SiO_2 coatings and change it from hydrophobic to hydrophilic. The ambient air plasma was generated by surface dielectric barrier discharge with a coplanar configuration of electrode system: Diffuse Coplanar Surface Barrier Discharge (DCSBD). The DCSBD unit can generate high-power-density surface plasma (100 W/cm^3) at low temperature of 70 °C (Homola et al., 2016). The RPS400 for roll-to-roll is compatible with state of the art roll-to-roll production and enables to quickly modify TiO_2/SiO_2 coatings on flexible substrates, without any damage to its bulk structure, which can find application in fast roll-to-roll manufacture (Ivanova et al., 2017, Homola et al., 2017).

2.3. Tested water

Firstly, the effect of hydrophobicity/hydrophilicity of TiO_2/SiO_2 coatings on photocatalytic decomposition of organic pollutants was studied using model solution of formic acid (50 mg L^{-1}) in distilled water.

Secondly, the efficiency of hydrophobic and hydrophilic TiO_2/SiO_2 thin films for solar water disinfection was tested in two different water matrixes. The first water matrix was bottled drinking water contaminated with natural consortia of fecal bacteria, prepared in accordance with recommendations of the World Health Organization in order to evaluate water treatment option (World Health Organization, 2011). Thus, influent from urban wastewater treatment plant (Conil de la Frontera, Cádiz) was used as a source of fecal bacteria. Before each photocatalytic solar disinfection test, bottled drinking water was inoculated with 1% (v/v) of wastewater influent. The second water matrix used for photocatalytic disinfection experiments was seawater with a relatively high concentration of potentially pathogenic bacteria. It should be noticed that autochthonous bacteria (*Vibrio* spp.) present in seawater in natural concentrations were used as a bacterial indicator in this case. This water was sampled from San Pedro Inlet (Puerto Real, Cadiz, Spain) and used for experiments without previous filtration. Characterisation of drinking water and seawater is presented in Table 1.

2.4. Experimental procedure for photocatalytic tests

2.3.1. Preliminary tests of photocatalytic activity

Preliminary experiments on mineralization of formic acid with TiO_2/SiO_2 thin films printed on flexible substrates were conducted in order to confirm the photocatalytic activity of

coatings. Formic acid was chosen as a model molecule because it is often found among ultimate compounds during degradation of various organic pollutants (Turki et al., 2013). Moreover, it was reported that photocatalytic decomposition of formic acid occurs without formation of any stable intermediates (Cornu et al., 2001, Turki et al., 2013). The photocatalytic decomposition of formic acid was performed using experimental set up shown in Figure 1. Photocatalytic experiments were performed in batch mode with recirculation. As can be seen from Figure 1, tubular borosilicate glass reactor (length 20 cm, diameter – 4.4 cm, volume 100 mL) was operated in closed circuit with recirculation. The glass tube (length 25 cm and diameter 3 cm) wrapped with photocatalytic thin film by Teflon tape was situated inside of tubular reactor. Model solution was recirculated using peristaltic pump (Percon N-M, JP Spectra). The total initial volume of model solution was 260 mL. The reactor was connected with stirred reservoir container. The light-emitting diodes (UVA-LEDs, 370 nm, length 30 cm and width 8 cm) lamp was located at distance of 1 cm from the surface of tubular reactor. The UVA intensity was measured on the reactor surface (irradiated) by means of UV AB Light Meter (General UV513AB). The intensity was 48 ± 0.6 W/m^2. Taking into account used experimental set up (Figure 1), it should be noted that only half of the tubular reactor was illuminated. Samples were taken at appointed time intervals. To achieve adsorption equilibrium first 30 min of contact time were carried out under continuous pumping in darkness. Samples (20 mL) were taken at required time intervals and analyzed by means of Total Organic Carbon (TOC) analyzer. The final volume of solution was measured in order to confirm the absence of evaporation.

2.3.2. Solar photocatalytic disinfection

All solar photocatalytic tests were conducted in borosilicate (BORO 3.3, ENDO glassware, volume 600 mL) batch vessel reactors under magnetic stirring. Before exposure to natural sun light, water in contact with tested coatings was agitated during 30 min (in absence of light). The total irradiated volume of water was 40 mL (height of water column 1 cm) and the geometrical surface area of thin films was 24 cm^2. All experiments were done under natural solar radiation during sunny days at the roof of INMAR-Marine Research Institute, University of Cádiz (36°31´43.6´´ N - 6°12´49.0´´ W). All tests were conducted in duplicate. The global UV radiometer CUV 5 (Kipp and Zonnen, the Netherlands) was used for measurements of UV solar radiation (280 - 400 nm). The cumulative UV dose (Q_{UV}, Wh/m^2) was estimated as shown below:

$$Q_{UV,t} = Q_{UV,t-1} + \Sigma(UV_t \cdot \Delta t) \quad (1)$$

where $Q_{UV,t}$ is the cumulative UV radiation dose received at each instant (Wh/m^2), UV_t is the UV radiation intensity recorded for certain time interval (W/m^2) and Δt is interval between measurements of radiation (h).

Solar disinfection (in absence of photocatalyst) and adsorption experiments (in absence of solar radiation) were performed as reference tests.

2.5. Chemicals and analytical methods

Formic acid 98% PA-ACS was purchased from Panreac. Membrane filtration (APHA, 2008) was used for monitoring of all target microorganisms. Water samples were taken at certain time intervals, filtered through 0.45 µm and then plated on Petri dishes using selective agar-based medium. For *Escherichia coli* (*E.coli*) and Total coliforms (T. coliforms), Chromogenic Colinstant Agar purchased from Scharlau was used. Slanetz-Barley Agar + TTC (1% v/v) (Panreac) and Thiosulfate Citrate Bile Salts Sucrose (TCBS) Agar were used for selective cultivation of *Enterococci* and *Vibrio* spp., respectively. Colonies were identified and counted after incubation during 24-48 h at 37 °C. The isolated colonies of *Vibrio* spp. were identified to species level by the amplification and sequentiation of a fragment of 16R rDNA. Briefly, this fragment was amplified using the universal primers SD-Bact-0008-a-S20 (5' AGA GTT TGA TCC CTC AG 3') and SD-Bact-1492-a-A-19 (5' GGT TAC CTT GTT ACG ACT T 3') (Kim and Austin, 2006). Polymerase chain reactions were carried out in a 50 ul reaction mixture that included 5 pmol of each primer, 100 uM dNTPs, 10X Dream taq PCR Buffer (includes 20mM MgCl2), 1 U Dream taq DNA Polymerase (Thermo Fisher Scientific) and 1 ul of genomic DNA. The PCR profile was as follows: 2 min at 95 ºC and 35 cycles of 30 s at 95 ºC, 40 s at 52 ºC and 1.3 min at 72 ºC and a final step 5 min at 72 ºC. Polymerase chain reaction products were electrophoresed on a 1% agarose gel and visualized via ultraviolet transilumination. The PCR products were sequenced by cycle sequencing using SDBact-0008-a-S20 and SD-Bact-1492-a-A-19 as a sequencing primer. Sequences were obtained on Sequence analyser (Genetic Analyzer ABIPRISM 310 Applied Biosystems). The sequences were aligned to the closest relative in the GenBank database using BLAST.

Concentration of cations and anions in fecally contaminated drinking water and marine water was measured by means of 882-Compact IC Plus (Metrohm; C4 250/4.0 column) ion chromatograph (IC) and 881-Compact IC Pro (Metrohm; ASupp5 250/4.0 column) equipped with conductivity detector. Mixture of CO_3^{2-} (3.20 mM) and HCO_3^- (1 mM) was used as an eluent for anion analysis (flow rate 0.7 mL/min), while HNO_3 (1.7 mM) and dipicolinic acid

$C_7H_5NO_4$ (0.7 mM) was an eluent for cation analysis (0.9 mL/min). The Titrando 905-Metrohm was utilized for analysis of carbonates and bicarbonates in drinking water. The pH of water was measured by means of Crison GLP 21 pH meter. Conductimeter Crison GLP 32 and hand refractometer ATAGO (S/Mill-E) were used for determination of conductivity and salinity of seawater, respectively. Transmittance of water in UVA range was measured with UV-visible spectrometer (Jenway 7315; Bibby Scientific, UK). The Shimadzu TOC-L analyzer in non-purgable organic carbon (NPOC) mode was utilized for measurement of TOC concentration in seawater. Presence of iron and dissolved titanium in water was analyzed using Thermo Iris Interpid, inductively coupled plasma atomic emission spectrometer (ICP-AES).

3. Results and Discussion

3.1. Characterization of prepared TiO_2/SiO_2 thin films

Morphology and homogeneity of TiO_2/SiO_2 were studied using scanning electron microscopy (SEM). The TiO_2/SiO_2 coatings treated by ambient air atmospheric pressure plasma were compared with not-treated thin films. Both types of coatings were porous and very homogeneous (Figure 2). It is noteworthy that microstructure of both types of coatings was very similar, confirming that plasma treatment does not affect the morphology of TiO_2/SiO_2 coatings (Homola et al., 2016). According to our observations, the size of the pores was in the range of 50 – 250 nm, which is in agreement with an earlier study (Homola et al., 2016).

The chemical composition of TiO_2/SiO_2 thin films (not treated and treated by ambient air atmospheric pressure plasma) was estimated utilizing EDX and XPS measurements. The results are presented in Figure 3 and 4, respectively. For EDX measurements, TiO_2/SiO_2 thin films were deposited on FTO glass substrate to avoid measuring the signal of the upper conductive layer necessary for SEM/EDX. The EDX results revealed that hydrophobic TiO_2/SiO_2 coating consisted of 16.5 at.% of titanium, 4.4 at.% of silicon and 66.7 at.% of oxygen. The concentration of carbon was 8.5 at.%. The EDX revealed minor concentration of tin (3.5 at.%) and possible concentration of fluorine (0.3 at.%) that originated from FTO substrate. The plasma-treated TiO_2/SiO_2 coating showed a similar atomic concentration of Ti, Si and O. The concentration of carbon was slightly lower and was found at 6.5 at.%.

Although the EDX is not the ideal technique for comparison of mesoporous coatings modified by plasma, the mapping mode straightforwardly showed the homogeneous

distribution of Ti, Si and O elements in the TiO_2/SiO_2 composite coatings. The plasma treatment had no significant effect on the spatial distribution of the elements within the coating.

The XPS was further used to provide a more reliable chemical characterization of the thin mesoporous coating. The penetration depth of XPS is significantly lower than EDX and it is more appropriate for surfaces treated by plasma, where changes after plasma treatment occur mainly on surfaces and not in the bulk.

Figure 4A shows the XPS survey spectra obtained from hydrophobic (untreated) and hydrophilic (plasma-treated) surfaces. The spectra showed peaks attributed to Ti 2p, Si 2p, O 1s, C 1s and Na 1s. The atomic concentrations calculated from the area under the peaks (the values are shown in Table 2) showed that both coatings differ significantly in the atomic concentration of carbon 1s. The hydrophobic TiO_2/SiO_2 coating showed C1s at 21.6 at.% whereas hydrophilic (plasm- treated) TiO_2/SiO_2 coating showed C1s at 5.7 at.%. The concentration of Ti 2p and Si 2p was not affected by plasma treatment, and concentration of O 1s increased proportionally with C 1s decrease. The decrease of C 1s and increase in O 1s signals are related to oxidation process induced by air plasma treatment. The presence of Na 1s can be explained by the content of sodium measured from soda-lime glass substrate. This indicates that mesoporosity of TiO_2/SiO_2 film significantly affects the penetration depth of XPS.

The XPS high-resolution C1s peak in Figure 4B shows a profound difference between hydrophobic and hydrophilic (plasma-treated) TiO_2/SiO_2 films. Both signals were referenced to C–C aliphatic bond at 284.8 eV and intensity of the signals were normalized to the highest value, thus both signals can be compared from their shape point of view. The ejected electrons with binding energies around 284.8 eV can be attributed to electrons from C–C or C–H bonds. The electrons with higher binding energies are bonded to electronegative element which is oxygen. The comparison of both signals showed that hydrophilic TiO_2/SiO_2 films have a higher amount of carbon bonded to oxygen (C–O, C=O, COOH). These bonds are polar and therefore make the surface hydrophilic.

Contact angle measurements confirmed the hydrophobic and hydrophilic nature of prepared TiO_2/SiO_2 coating. Thus, for hydrophobic coatings, the mean contact angle was $126.4^o \pm 1.3^o$, while for hydrophilic it was $11.9^o \pm 0.8^o$. Images of water droplets on the surface of hydrophobic and hydrophilic coatings are shown in Figure 5.

Since the water droplet deposited on the TiO_2/SiO_2 surface treated by plasma was quickly absorbed by the coating, which confirms its mesoporosity and hydrophilicity, a dynamic water uptake study was employed to provide a comparison between hydrophobic and hydrophilic coatings. Figure 6 shows the comparison of total force acting on a sample brought into contact with water surface and observed for 40 seconds. The hydrophobic sample brought into contact with water surfaces was immediately repealed from the water surface, which was characterized by a buoyant force acting on the sample. The value of the force was -2 mN at the time when the sample was brought into contact with the water surface. After several seconds, the total force acting on the sample slightly increased, which can be related to slight absorption of the water in the film, possibly due to the interaction of backside PET surface with the water surface.

On the other hand, the hydrophilic sample (plasma-treated) showed opposite behavior when brought into contact with the water surface. The total force acting on the sample increased rapidly, which can be explained only with the increased weight of the sample ($F = m \times g$). The increase in weight can be directly understood as absorption of the water within the mesoporous TiO_2/SiO_2 coating. The absorption and the total force reached the maximum after 10 s at 3.5 mN. The remained contact of the sample with water surface did not affect further increase of the absorption. More detailed characterization of used in this study thin films was reported elsewhere (Homola et al., 2016).

3.2. Preliminary photocatalytic activity testing

Photocatalytic mineralization of formic acid in aqueous solution with an initial concentration of 50 mg/L was performed using prepared hydrophilic and hydrophobic TiO_2/SiO_2 coatings on flexible substrate. Samples were taken at appointed time intervals and analyzed by means of TOC analyzer. To achieve adsorption equilibrium first 30 min of contact time were carried out under continuous pumping in darkness (UV off in Figure 7). No pretreatment of TiO_2/SiO_2 thin films was applied before photocatalytic tests. No evaporation of tested model solution was detected.

From Figure 7 it can be seen that prepared TiO_2/SiO_2 thin films can be successfully used as photocatalysts. However, at chosen experimental conditions, initial degradation rate of formic acid is similar for hydrophobic and hydrophilic coatings.

Grégori et al. (Gregori et al., 2014) reported about the twice higher photocatalytic activity of hydrophilic TiO_2/SiO_2 thin films (after UV treatment) towards formic acid decomposition as

compared to hydrophobic ones. Taking into consideration high efficiency of UVA-LED lamp used in our experiments, it can be suggested that "self-cleaning" step of hydrophobic coating occurred relatively fast in the beginning of photocatalytic process. After "self-cleaning" step hydrophilicity of hydrophobic coating increased and similar photocatalytic activity towards formic acid was achieved as compared to hydrophilic thin film.

3.3. Solar photocatalytic inactivation of natural bacteria consortia in drinking water

Solar disinfection tests were performed using hydrophilic and hydrophobic TiO_2/SiO_2 thin films and inactivation of typical indicators of fecal contamination in drinking water (*E.coli*, T. coliforms and *Enterococci*) was monitored. SODIS test (in absence of photocatalyst) was conducted as a reference as well as adsorption tests (in absence of solar radiation). Results of fecal bacteria inactivation (log scale) as a function of UV dose (UVB and UVA) are presented in Figure 8. Hydrophilic TiO_2/SiO_2 coatings under solar radiation demonstrated similar to SODIS efficiency for *E.coli* inactivation (Figure 8A). Interestingly, hydrophobic thin films were slightly more efficient than hydrophilic ones by reaching 0.48 log removals greater at 22.05 Wh/m^2. This observation can be explained by the fact that adhesion of *E.coli* on hydrophobic TiO_2/SiO_2 coatings was slightly higher than on hydrophilic ones, as observed in adsorption tests (Figure 8A, inset). In case of T. coliforms and *Enterococci* no significant difference was observed between SODIS and solar photocatalytic disinfection, indicating efficiency of SODIS for inactivation of fecal bacteria in drinking water. As can be seen from Figure 8, sensitivity of chosen species to SODIS and solar photocatalytic disinfection varied. Based on the dose necessary to reach the detection limit, the trend *E.coli* (22.05 Wh/m^2) < T. coliforms (33.40 Wh/m^2) < *Enterococci* (44.91 Wh/m^2*)* was obtained, which is in agreement with earlier studies (Levchuk et al., 2018, Rincón and Pulgarin, 2004a, van Grieken et al., 2010, Dalrymple et al., 2010).

As reported in earlier studies on photocatalytic disinfection, as power of bacteria adhesion on the surface of photocatalytic material increase so does the efficiency of photocatalytic bacteria inactivation (Tallósy et al., 2016). Thus, the adhesion onto photocatalyst surface is positively correlated to the inactivation efficiency (Pablos et al., 2013). Several parameters can affect the adhesion onto the photocatalyst surface such as the chemical composition of water and cell wall characteristics.

It is generally accepted that highly oxidizing species, such as hydroxyl radicals, are generated during photocatalysis. Due to very short lifetime these species most probably are

available on the surface of the photocatalytic coatings. Therefore, it is logical that hydrophobic TiO_2/SiO_2 coatings, which possess higher adhesion capacity for bacteria, are more efficient for inactivation. According to earlier studies, hydroxyl radicals are responsible for oxidation of bacteria's cell wall, leading to the loss of bacteria viability (Kiwi and Nadtochenko, 2005, Kubacka et al., 2014). In this sense, and assuming that there are no differences in the isoelectric behavior between gram-negative and gram-positive bacteria (Pablos et al., 2013), the faster inactivation of gram-negative is due to the reactivity of cell wall components with radical generated (Dalrymple et al., 2010, van Grieken et al., 2010)

Morphological changes of natural bacteria consortia were monitored before and after solar photocatalytic disinfection tests by means of SEM. The SEM images of pathogenic bacteria before and after disinfection are shown in Figure 9. As shown in Figure 9 (A, B, C and D), the morphology of pathogenic bacteria prior solar photocatalytic disinfection is undamaged and smooth. However, after photocatalytic disinfection clear damage of microorganisms was observed (Figure 9E, F and G), which indicates the efficiency of this process. Interestingly, deformation of the bacteria adhered on the TiO_2/SiO_2 surfaces was observed, such as stretching of bacteria cell walls (Figure 9H) especially in the pores of the nanostructured surface. The degree of membrane stretching was reported as a crucial parameter for antimicrobial surfaces (Elbourne et al., 2017).

Taking into consideration possible application of TiO_2/SiO_2 coatings for inactivation of pathogenic bacteria in drinking water, leaching of photocatalyst was studied by means of ICP-AES. Water samples after photocatalytic solar disinfection were collected and each sample was measured in triplicate. The concentration of titanium in water after experiments with hydrophobic and hydrophilic coatings was 1.24 ± 0.04 µg/L and 19.00 ± 3.00 µg/L, respectively. Obtained results were in agreement with XPS measurements conducted using TiO_2/SiO_2 coatings collected after water disinfection. Thus, it was observed that atomic concentration of Ti in hydrophobic coating was very similar to fresh coating (8.6 at.%), while significant decrease of titanium concent was observed for hydrophilic films after water treatment (4.4 at.%). Hence, higher leaching of titanium from hydrophilic TiO_2/SiO_2 thin films was observed, and thus can also influence on higher inactivation rates on bacteria due to photocatalysis, by comparison with SODIS.

3.4. Solar photocatalytic inactivation of pathogenic marine bacteria in seawater

For solar photocatalytic disinfection of seawater, *Vibrio* spp. was chosen as a target bacteria because it can be often found in marine aquaculture effluents (Oxley et al., 2002) and some

species of *Vibrio* genus can be pathogenic for marine organisms and human (Plaza et al., 2017).

Identification of *Vibrio* spp. present in seawater (characterization is shown in Table 1) was conducted by cultivation of *Vibrio* spp. using growth medium (TCBS agar) and subsequent isolation of typical green and yellow colonies. Isolated colonies were identified as *Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio alginolyticus*. *Vibrio alginolyticus* includes pathogenic strains for aquaculture organisms and for human (Plaza et al., 2017).

Results of solar photocatalytic inactivation of *Vibrio* spp. (*Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio harveyi*) with hydrophobic and hydrophilic TiO_2/SiO_2 thin films deposited on flexible substrate are shown in Figure 10. Both types of TiO_2/SiO_2 coatings accelerate the inactivation of *Vibrio* spp. in comparison with SODIS. At 90 min. (65 Wh/m^2) an improvement of 19% (hydrophilic) and 27% (hydrophobic) was achieved (based on Log reductions). Thus, inactivation of *Vibrio* spp. was faster when hydrophobic TiO_2/SiO_2 was used. Based on the adsorption tests (Figure 10, inset), this can be probably attributed to slightly higher adhesion of *Vibrio* spp. to hydrophobic TiO_2/SiO_2 as compared with hydrophilic one. As gram-negative bacteria, similar cell wall characteristics as *E. coli* can be expected. Otherwise, the solution chemistry differ from drinking water matrix: seawater is a highly complex solution, with a significant content of ions, so both the ionic strength and the chemical composition of water can also have an effect on the adhesion onto the photocatalyst surface (Gogniat et al., 2006, Poortinga et al., 2002). Based on obtained results, it can be suggested that hydrophobic TiO_2/SiO_2 coatings are efficient for inactivation of potentially pathogenic marine bacteria by solar photocatalysis. Inactivation rate of *Vibrio fischeri* was studied in artificial seawater using Fe_2O_3-TiO_2 nanoparticles under UVA and visible light (Baniamerian et al., 2018). It was reported that at optimal conditions (1 g/L of Fe_2O_3-TiO_2, 2.5 wt% of Fe_2O_3) almost complete inactivation (99.4%) of *Vibrio fischeri* was achieved after 4 h under visible light, while under UVA only 0.5 h was needed (Baniamerian et al., 2018). It is difficult to compare these results with our study, especially taking into account differences in such crucial parameters as experimental conditions, concentration of bacteria, type of radiation and photocatalyst. However, considering that light intensity was reported to be 55 W/m^2 (Baniamerian et al., 2018), we can estimate that UV dose required for inactivation of bacteria achieved in study of Baniamerian et al. (2018) under UVA light was more than two times lower than in this study. In another study, the complete inactivation of two different marine strains was achieved after 60 min (for the most resistant strain) at

experimental conditions of 100 mg/L of TiO_2, 0.334 mW/cm^2 UVA (Leung et al., 2008). Taking into consideration that relatively few studies reported results of seawater disinfection (Moreno-Andrés et al., 2017a, Moreno-Andrés et al., 2018b, Rubio et al., 2013), it is of great interest to compare efficiency of solar photocatalysis with other solar-driven disinfection methods. Thus, combination of SODIS with H_2O_2 was reported as an efficient treatment for inactivation of *Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio harveyi* in seawater (Villar-Navarro et al., 2019). For complete inactivation of *Vibrio* spp. by SODIS/H_2O_2 at optimal conditions (1 mg/L of H_2O_2) the UV dose of 33.4 Wh/m^2 was required (Villar-Navarro et al., 2019), which is about two times lower than UV dose required of *Vibrio* spp. inactivation by solar photocatalysis.

Results of *E. coli*, T. coliforms and *Enterococci* inactivation in drinking water by solar photocatalysis were very similar to SODIS (Section 3.3), while *Vibrio* spp. inactivation was significantly enhanced when TiO_2/SiO_2 thin films were used. This observation can probably be explained by the fact that *E.coli*, T. coliforms and *Enterococci* are not autochthonous bacteria in drinking water and, therefore, can be easily inactivated using only solar light (Giannakis et al., 2014). While the case of *Vibrio* spp. in seawater is different. *Vibrio* spp. are autochthonous bacteria in seawater, hence, only SODIS is not that efficient for its inactivation. Therefore, the introduction of TiO_2/SiO_2 coatings (solar photocatalytic disinfection) significantly enhance inactivation of *Vibrio* spp. In addition, a major sensitivity for fecal organisms in comparison with wild marine bacteria can be noticed (Figure 8 and 10). Even difference in kinetics can be perceptible, thus, a typical "shoulder" appears for *Vibrio* spp. and not for fecal microorganisms. Such differences in sensitivity of microorganisms are in agreement with other studies (Moreno-Andrés et al., 2018a).

Taking into consideration efficiency of photocatalytic disinfection for inactivation of *Vibrio* spp. in seawater it can be considered as a promising method for disinfection of aquaculture effluents (Villar-Navarro et al., 2019), ballast water (Moreno-Andrés et al., 2017b), etc. However, the efficiency of photocatalytic coatings may be significantly affected by relatively high salinity of the water. The efficiency of *Vibrio* spp. inactivation in seawater using hydrophobic TiO_2/SiO_2 was studied during ten cycles. After each test, fresh seawater was added to the reactor. The photocatalytic films were not rinsed between cycles. Results are shown in Figure 11.

Interestingly, a decrease of photocatalytic disinfection using hydrophobic TiO_2/SiO_2 was observed after ten cycles (15 h of exposure to seawater). Rubio et al. (Rubio et al., 2013)

reported 50% decrease of photocatalytic activity of immobilized TiO_2 after exposing to seawater during 107 h. Loss of photocatalytic activity during solar inactivation of *Vibrio* spp. using TiO_2/SiO_2 films can be possibly explained by deposition of salts on the surface of photocatalytic material. The SEM images were taken after one photocatalytic cycle (Figure 11) and visual observation of TiO_2/SiO_2 coating after experiments confirmed deposition of salts on the coating's surface. According to the literature (Abdullah et al., 1990), active sites of photocatalyst can be blocked by chloride ions, which abound in seawater. Another possible reason for decrease of photocatalytic activity in seawater is scavenging effect of chloride ion towards oxidizing radicals (·Ox) (Abdullah et al., 1990) as shown in the reaction (2).

$$\cdot Ox + Cl^- \rightarrow Cl\cdot + Ox^- \quad (2)$$

Moreover, negative effect of other anions, for instance hydrogen carbonate (HCO_3^-) that are present in seawater on photocatalytic disinfection was reported (Rincón and Pulgarin, 2004b). According to the literature (Rincón and Pulgarin, 2004b), HCO_3^- can react with hydroxyl radicals resulting in $CO_3^{\cdot -}$, which decrease the reaction rate.

$$\cdot OH + HCO_3^- \rightarrow CO_3^{\cdot -} + H_2O \quad (3)$$

$$\cdot OH + CO_3^{2-} \rightarrow CO_3^{\cdot -} + OH^- \quad (4)$$

The salinity of seawater used in our experiments was 36 ‰. In spite of high salinity, the inactivation of wild *Vibrio* spp. (*Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio harveyi*) by solar photocatalysis with hydrophobic TiO_2/SiO_2 thin films was efficient. The decrease of photocatalytic activity of TiO_2/SiO_2 coating can be prevented by washing the surface with pure water as demonstrated in earlier studies (Kabra et al., 2004).

4. Conclusions

In this study, hydrophobic and hydrophilic composite TiO_2/SiO_2 thin films were deposited on a flexible substrate and tested for solar photocatalytic disinfection of seawater and drinking water with fecal contamination. Inactivation of *E.coli*, T. coliforms and *Enterococci* (drinking water) and *Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio harveyi* (seawater) was studied. Main outcomes are shown below.

- Hydrophobic and hydrophilic TiO_2/SiO_2 coatings were equally efficient for photocatalytic decomposition of formic acid.

- The efficiency of pathogenic bacteria (*E.coli*, T. coliforms) inactivation in drinking water with fecal contamination by solar photocatalysis was slightly higher than solar disinfection (SODIS). However, similar results were obtained for inactivation of *Enterococci* using SODIS and solar photocatalytic disinfection. Based on these results it can be suggested that solar photocatalytic disinfection with TiO_2/SiO_2 thin films is related to the bacterial adhesion, and does not significantly enhance inactivation efficiency of bacteria, which can be considered as very sensitive to SODIS.
- Inactivation of *Vibrio* spp. (*Vibrio owensii*, *Vibrio alfacsensis* and *Vibrio harveyi*) in seawater was faster when solar photocatalysis was applied in comparison with SODIS. Moreover, hydrophobic TiO_2/SiO_2 thin films were more efficient that hydrophilic ones, which was attributed to higher bacteria adhesion capacity of hydrophobic coatings. Efficiency of hydrophobic TiO_2/SiO_2 thin films was studied during ten cycles and decrease of photocatalytic activity was observed, attributed to deposition of salts on the surface of the coating.
- It was observed that autochthonous bacteria such as *Vibrio* spp. in seawater are more resistant to inactivation by SODIS in comparison with not autochthonous bacteria such as *E.coli*, T. coliforms and *Enterococci* in contaminated drinking water. Hence, it can be suggested that hydrophobic TiO_2/SiO_2 thin films can be promising for inactivation of autochthonous pathogenic bacteria under natural solar radiation.

Hydrophobic ink-jet printed TiO_2/SiO_2 thin films are attractive photocatalytic materials, mainly due to the possibility to print these films on flexible substrates and prepare coatings of large area, which can be suitable for any reactor type. Results of this study suggest that printed TiO_2/SiO_2 coatings are promising for solar photocatalytic inactivation of pathogenic marine bacteria in seawater, which can be applied as an alternative disinfection method for aquaculture effluents. However, appropriate cleaning procedure for photocatalyst should be studied in order to check feasibility of printed TiO_2/SiO_2 for real-world application. Moreover, the combination of solar photocatalysis with relatively low concentrations of H_2O_2 could further decrease disinfection time, which will be conducted in our future works.

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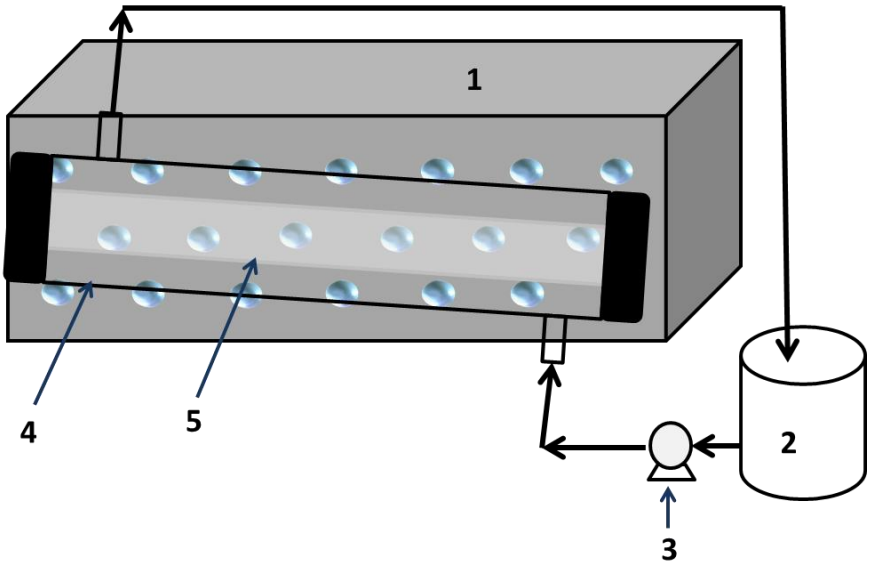
Table 1. Characterization of fecally contaminated drinking water and seawater			
Fecally contaminated drinking water		*Seawater*	
Parameter (unit)	**Value**	**Parameter (unit)**	**Value**
Na^+ (mg/L)	4.1 ± 0.1	Na^+ (g/L)	11.53 ± 0.05
Cl^- (mg/L)	4.7 ± 0.1	Cl^- (g/L)	20.80 ± 0.01
Ca^{2+}(mg/L)	6.15 ± 0.1	Ca^{2+}(mg/L)	0.53 ± 0.001
Mg^{2+} (mg/L)	0.65 ± 0.1	SO_4^{2-}	2.30 ± 0.13
HCO_3^- (mg/L)	0.99 ± 0.1	Conductivity (mS/cm)	48 ± 5
Transmittance (280 – 400 nm, %)	95.5	Transmittance (280 – 400 nm, %)	96
E.coli (CFU mL^{-1})	10^2	*Vibrio* spp. (CFU/1 mL)	10^2
Total coliforms (CFU mL^{-1})	10^2-10^3	TOC (mg/L)	2 ± 1
Enterococci (CFU mL^{-1})	10^2	Salinity (‰)	36
pH	7.3	pH	8
Fe (µg L^{-1})	<D.L.	Fe (µg/L)	11.2 ± 4

Table 2. Atomic concentration of elements of the hydrophobic and hydrophilic TiO_2/SiO_2 thin films obtained from XPS measurements

Sample	C1s	O1s	Ti2p	Si2p	Na1s
Hydrophobic	21.63	50.34	9.28	16.48	2.27
Hydrophilic	5.43	64.10	9.46	16.38	4.63



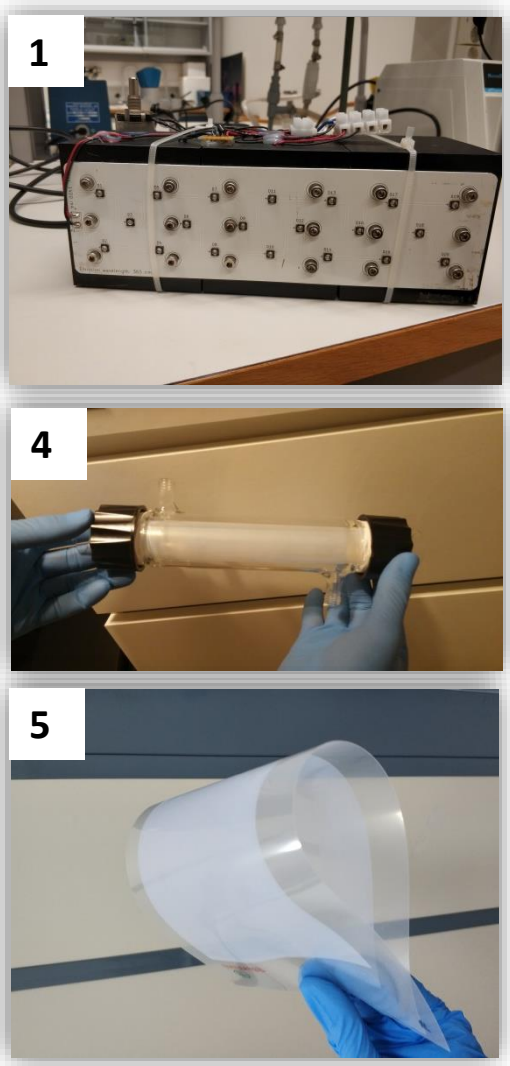


Figure 1. Experimental set up; 1 – UVA-LEDs (370 nm) lamp; 2 – reservoir; 3 – peristaltic pump; 4 – tubular borosilicate glass reactor; 5 – TiO_2/SiO_2 thin film deposited on flexible PET support

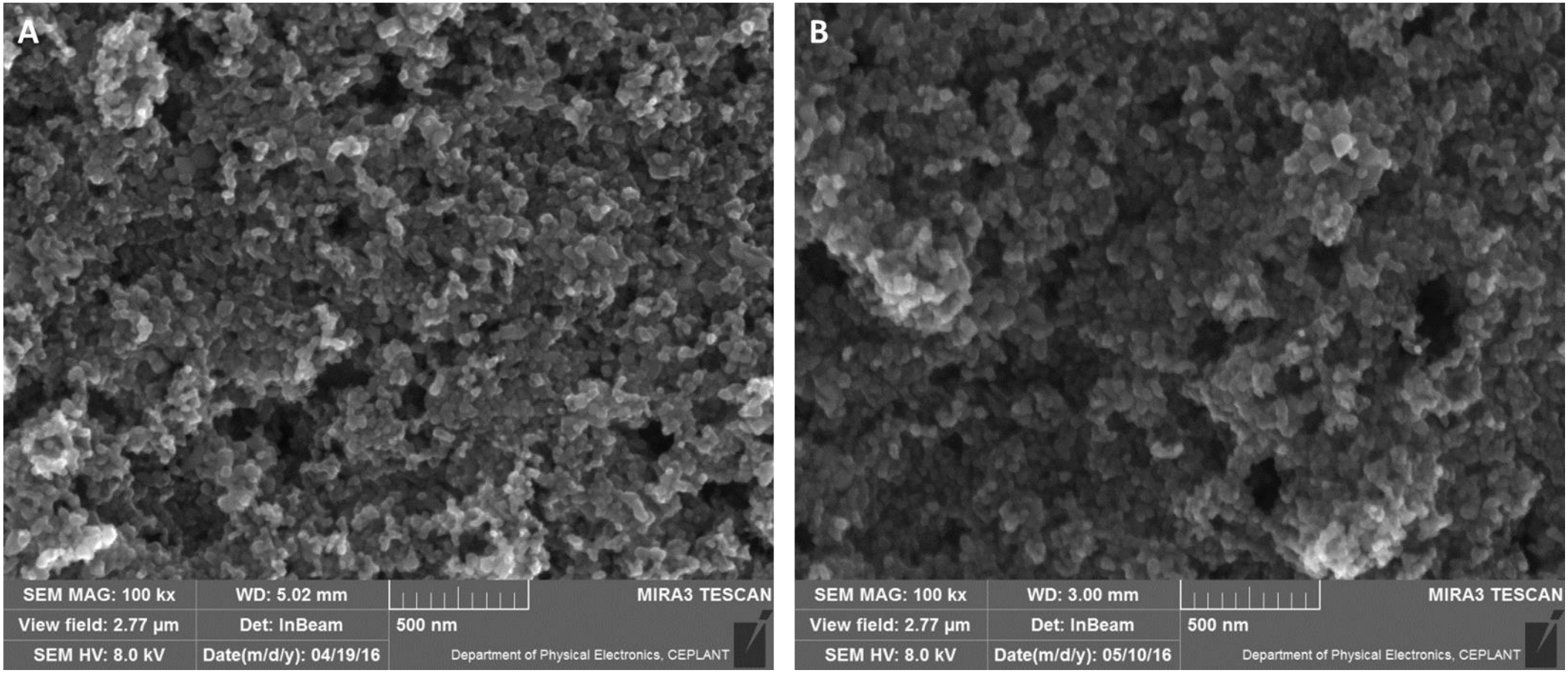


Figure 2. SEM images of hydrophobic (A) and hydrophilic (B) TiO_2/SiO_2 coatings deposited on flexible substrate

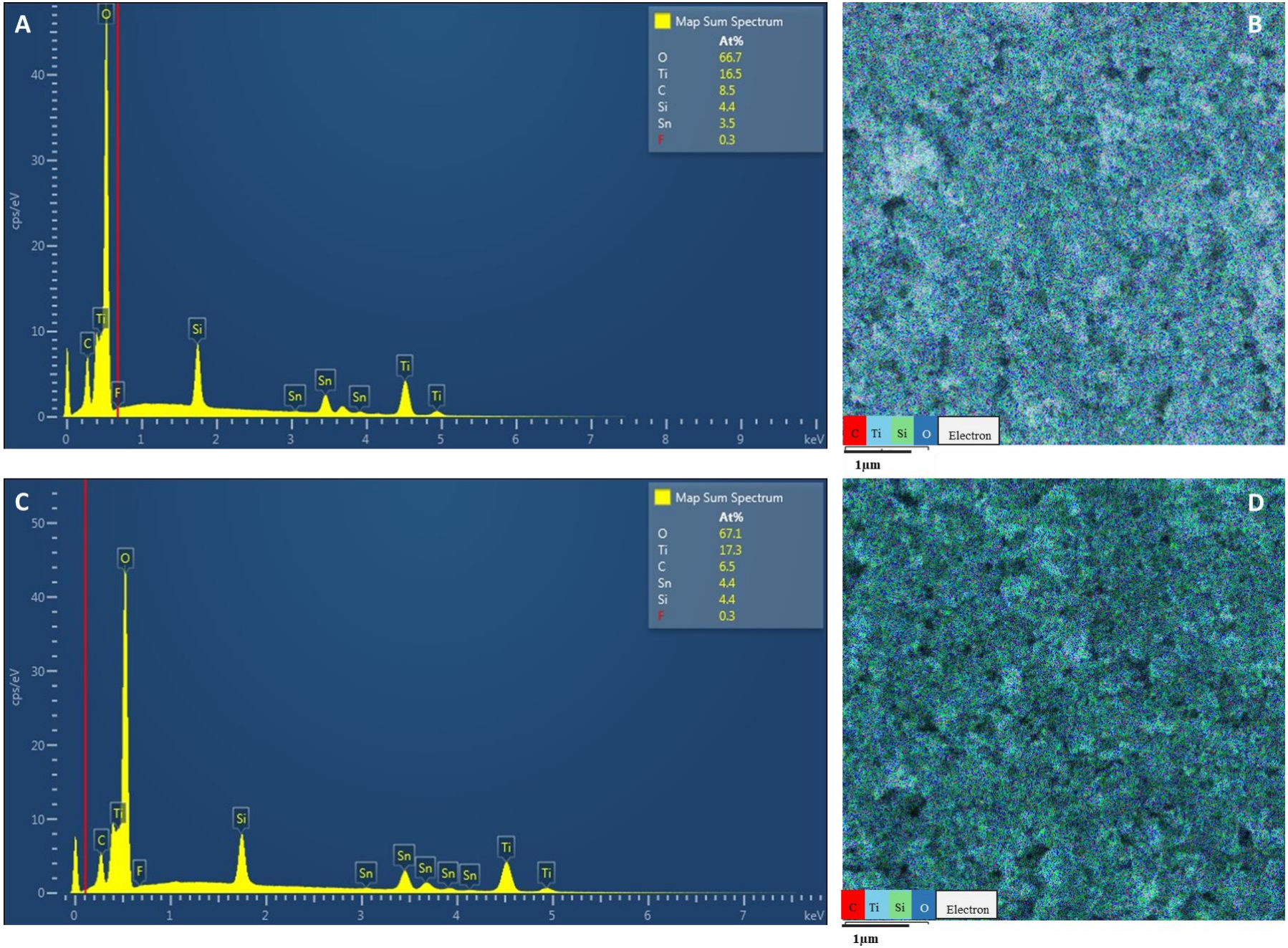


Figure 3. EDX and mapping of hydrophobic (A, B) and hydrophilic (C, D) TiO_2/SiO_2 coatings

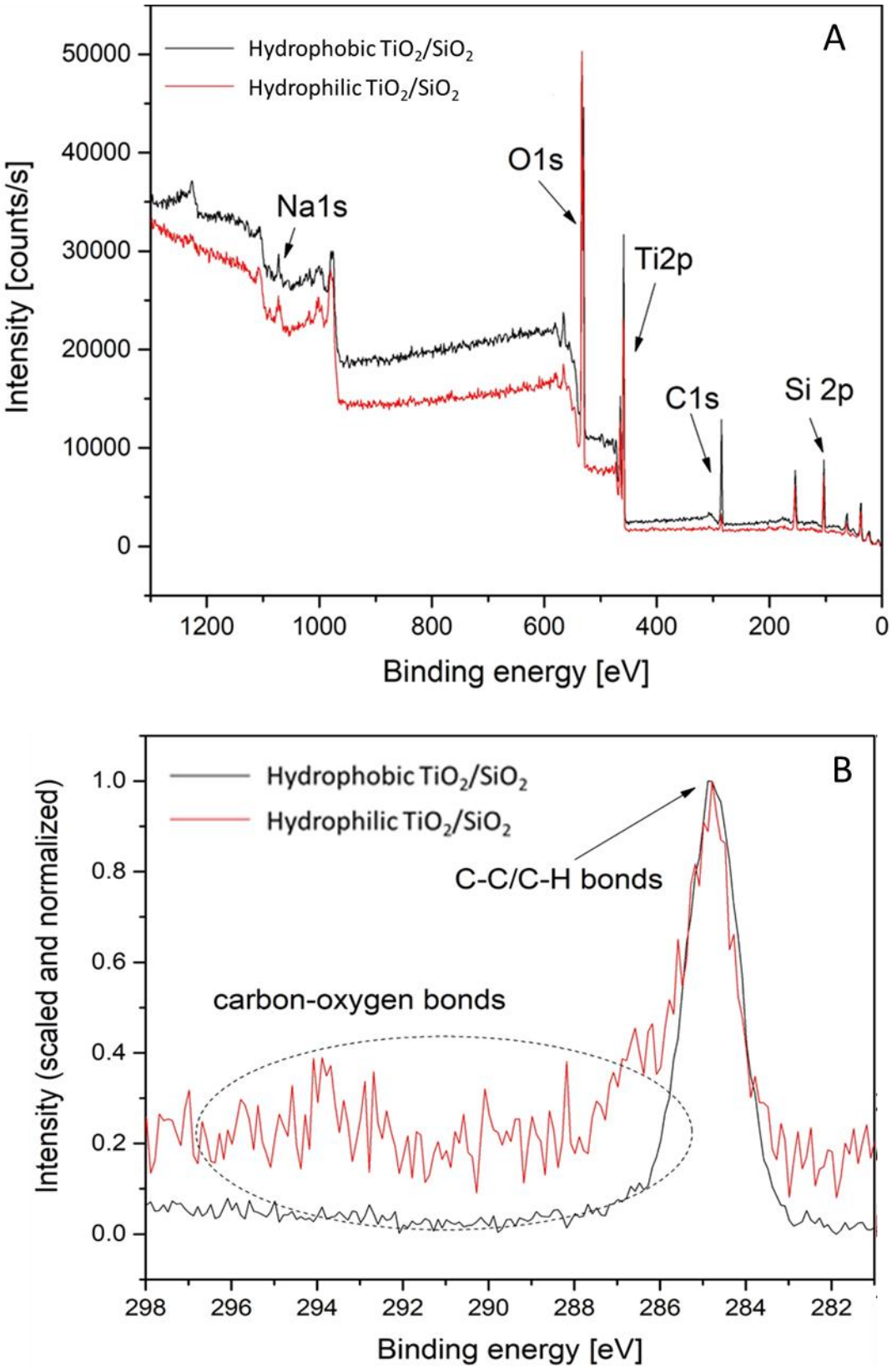


Figure 4. A – Typical XPS spectra of hydrophobic and hydrophilic TiO_2/SiO_2 coatings, B – comparison of C1s peak of hydrophobic and hydrophilic TiO_2/SiO_2 films

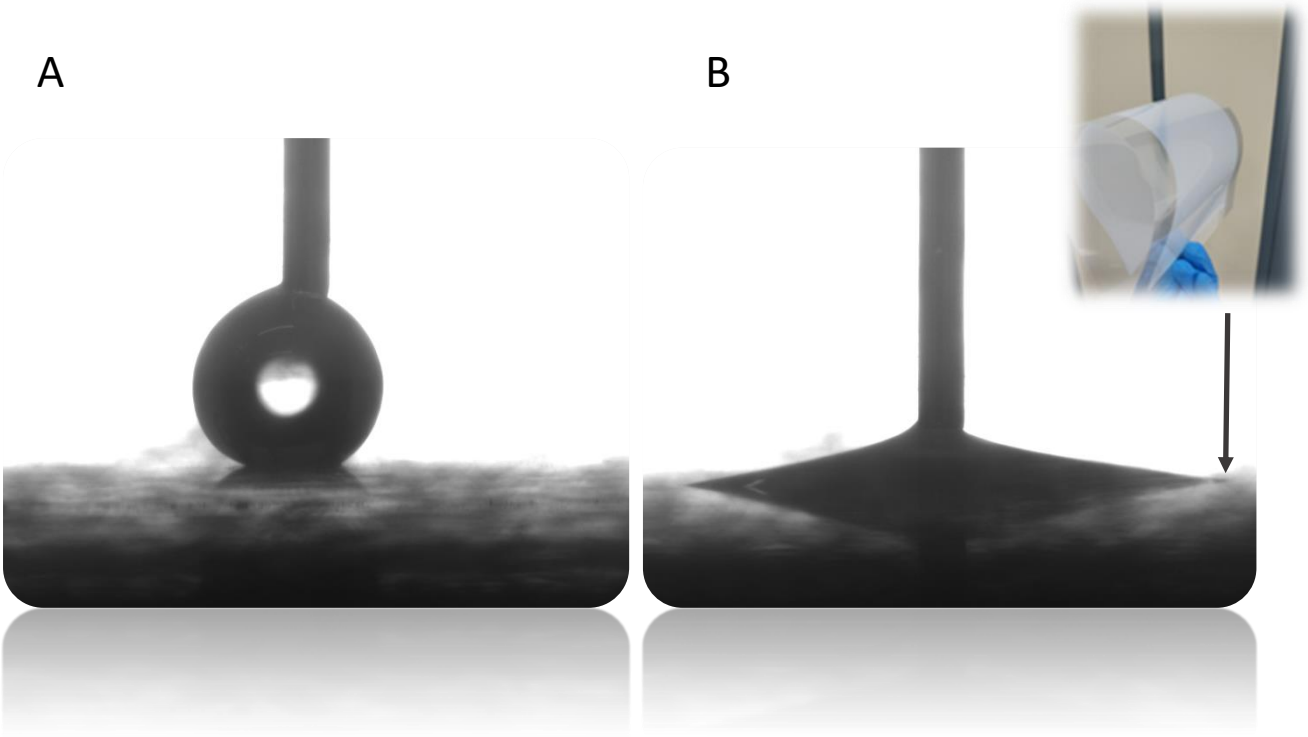


Figure 5. Images of water droplets on the surface of hydrophobic (A) and hydrophilic (B) TiO_2/SiO_2 thin films deposited on flexible substrate

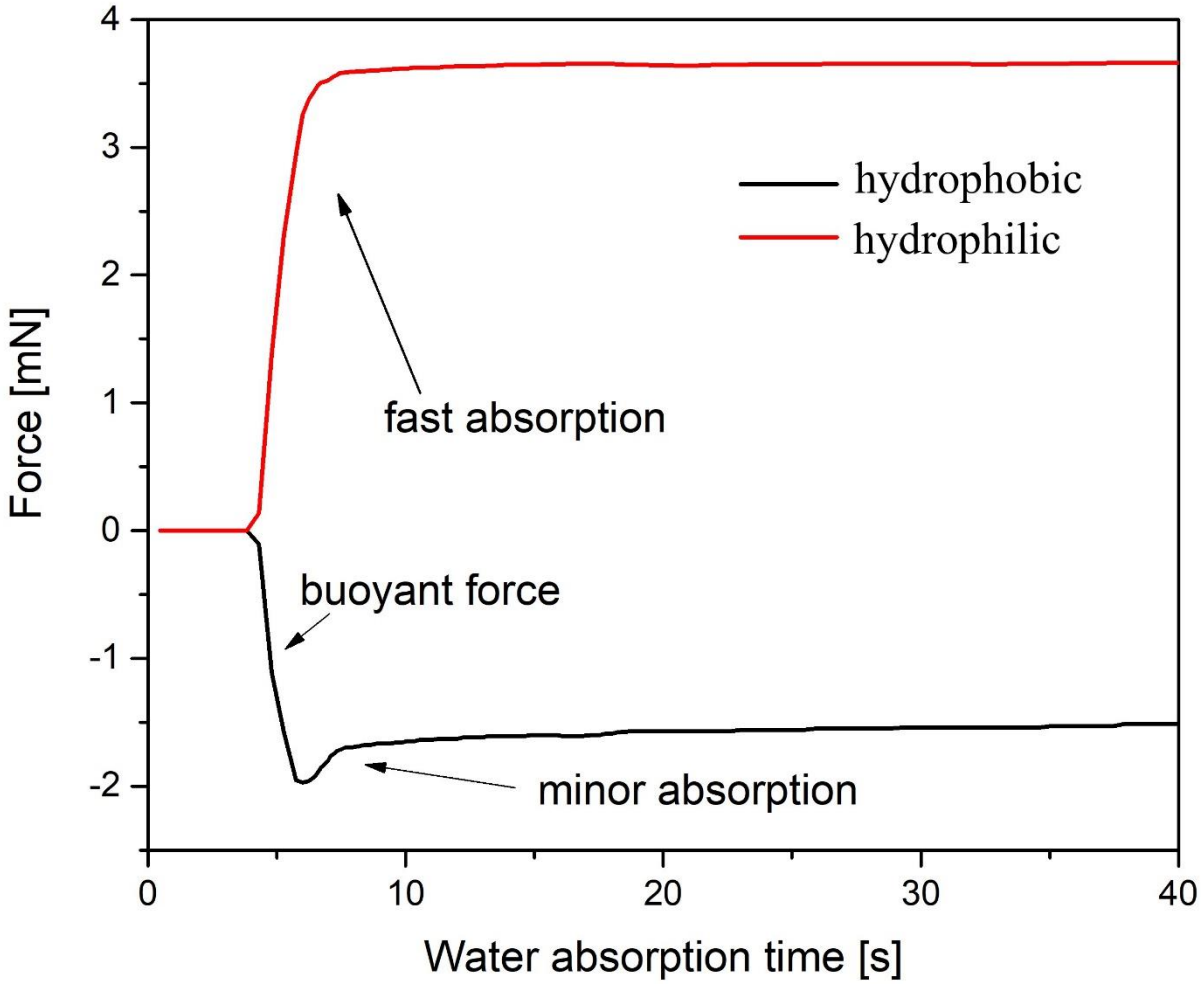


Figure 6. Results of water uptake study for hydrophobic and hydrophilic surfaces

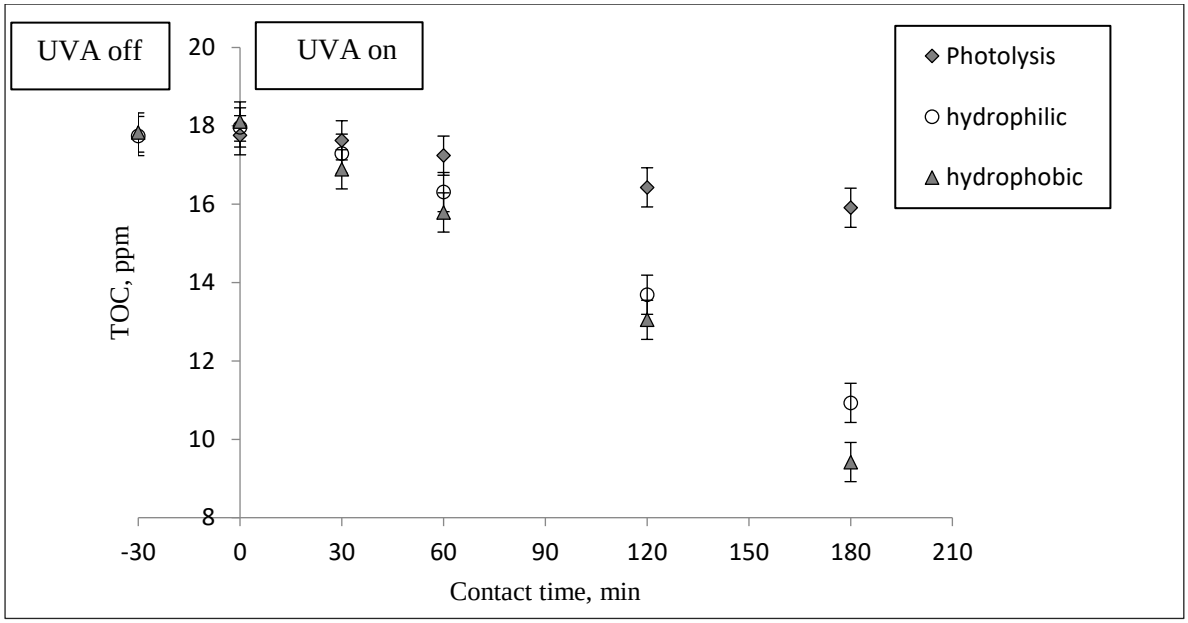


Figure 7. Results of photocatalytic decomposition of formic acid in water using hydrophobic and hydrophilic TiO_2/SiO_2 thin films

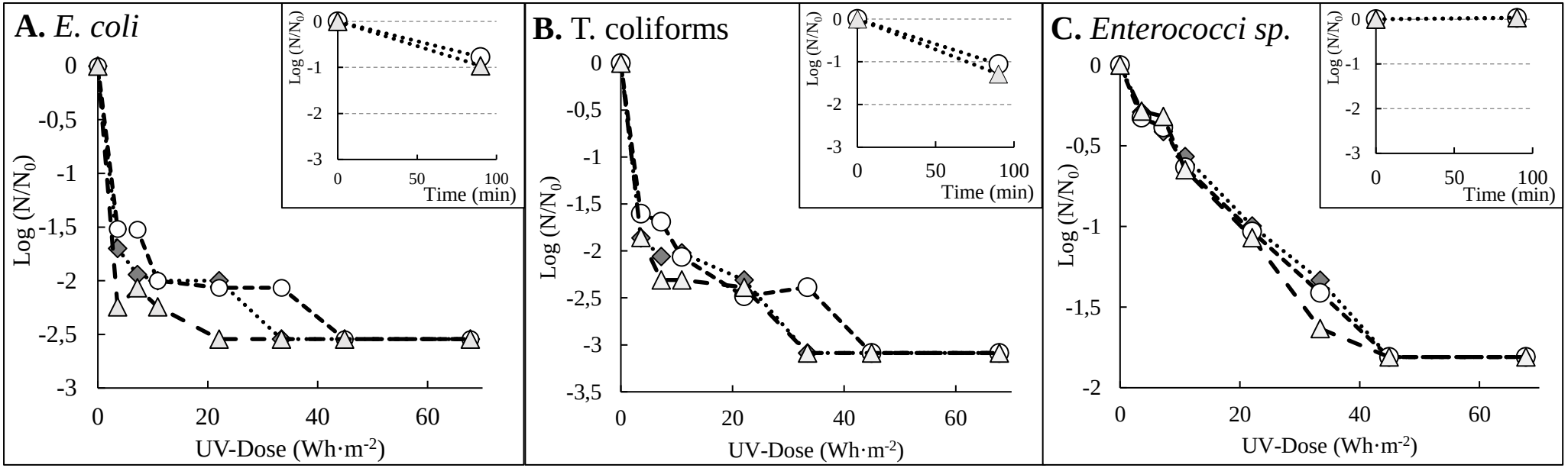
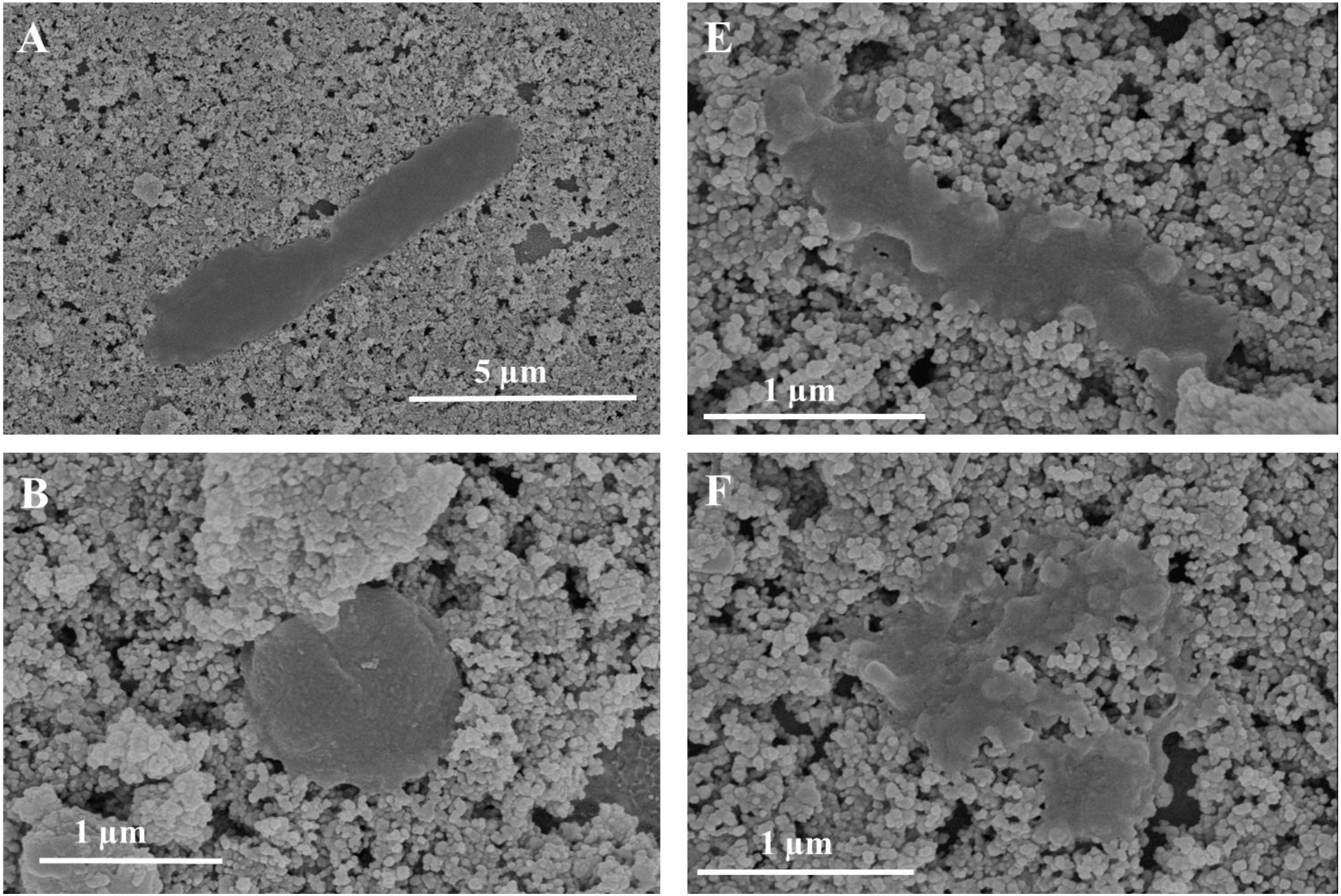


Figure 8. Inactivation of fecal bacteria in drinking water by SODIS (♦), solar photocatalysis on hydrophilic surface (○) and solar photocatalysis on hydrophobic surface (▲). The inset of each Figure represents the log-reduction obtained by adhesion of bacteria to coatings in darkness (reference test) during the experiment time. Each experimental point represents a mean value with coefficient of variation less than 30%.


A
5 µm
E
1 µm
B
1 µm
F
1 µm

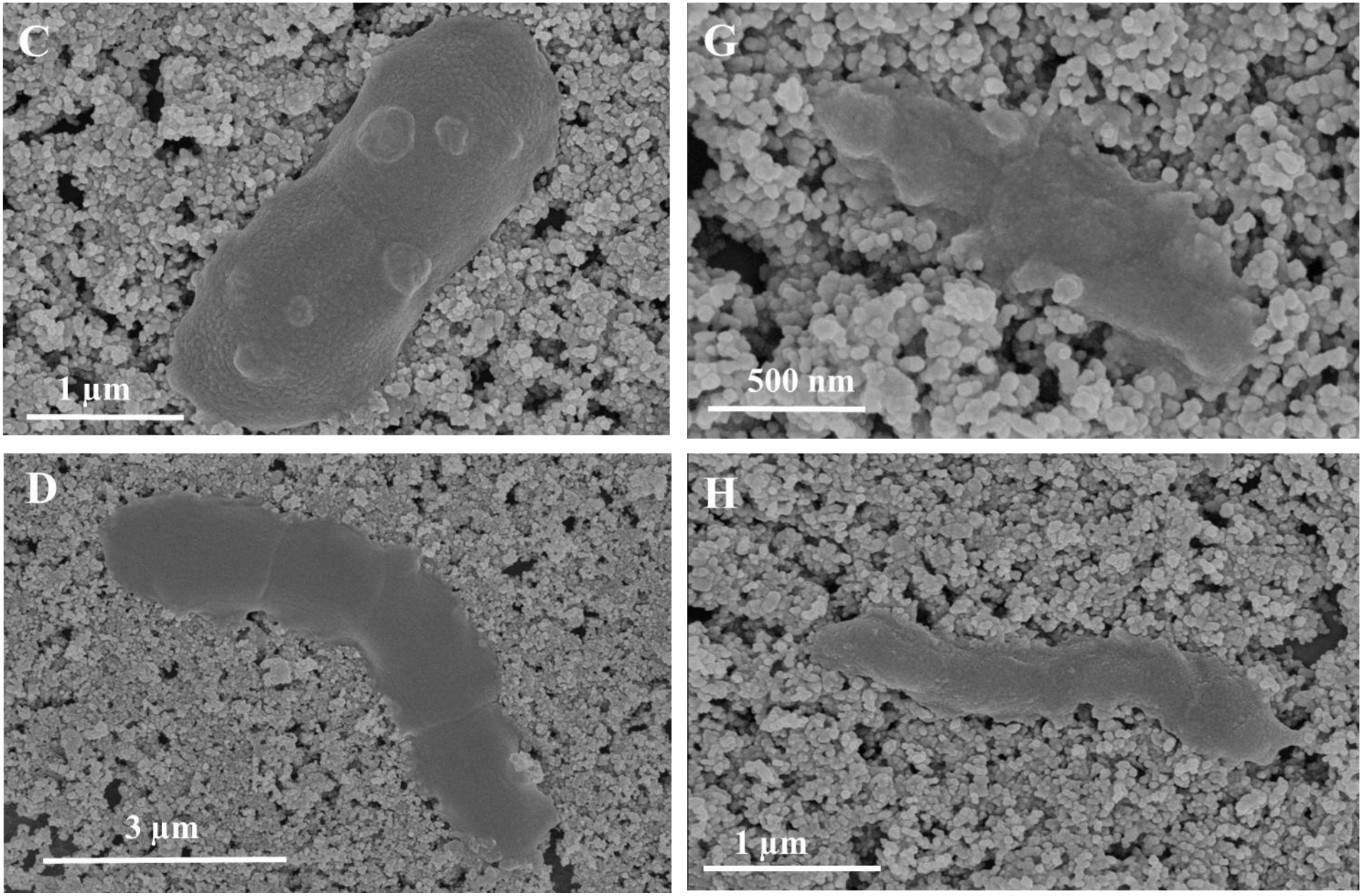


Figure 9. SEM images of various wild bacteria on the surface of hydrophobic and hydrophilic TiO_2/SiO_2 thin films before (A, B, C, D, H) and after photocatalytic disinfection (E, F, G); A - E, B – F, D – hydrophilic TiO_2/SiO_2 thin films and C – G and H – hydrophobic TiO_2/SiO_2 thin films

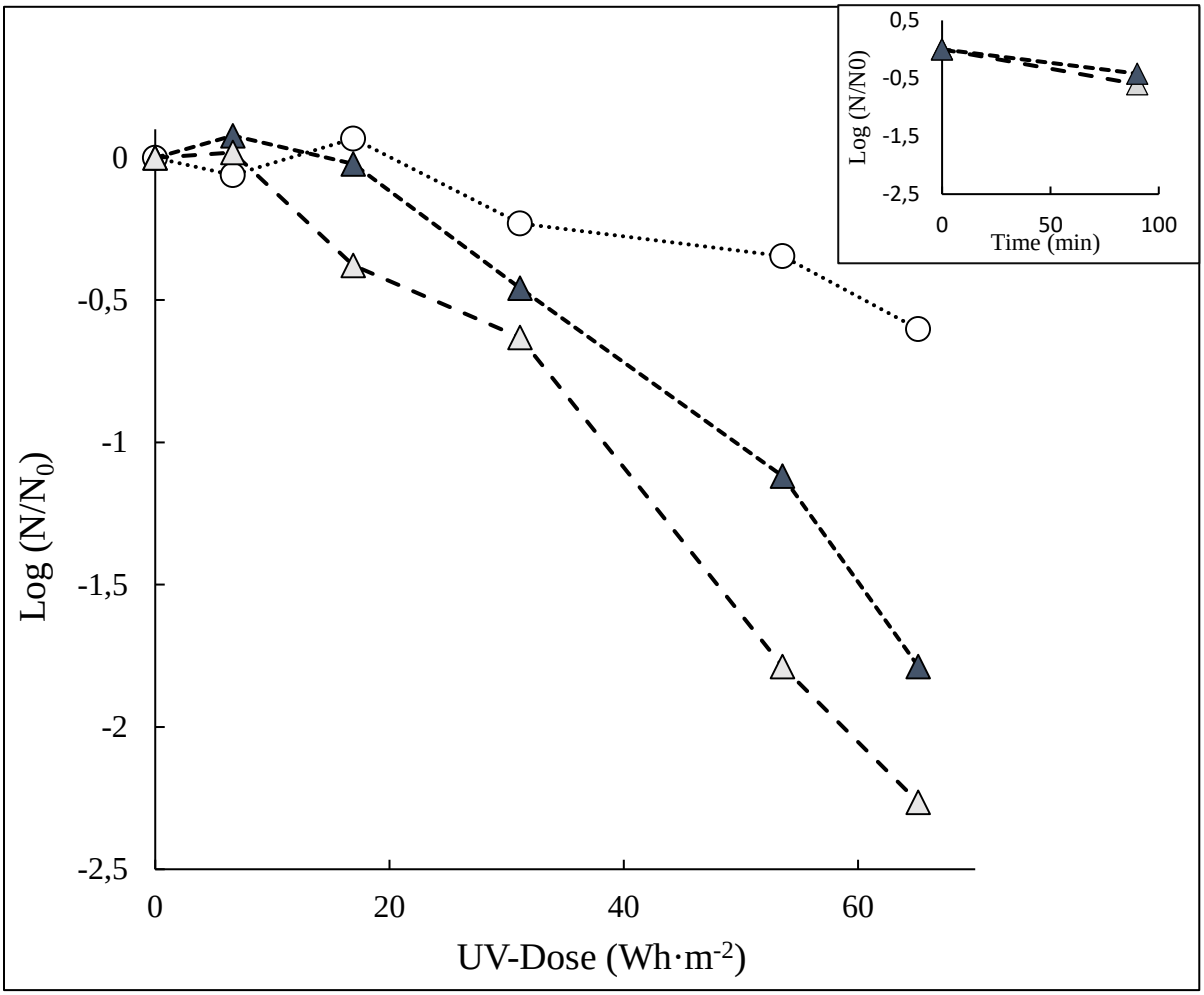


Figure 10. Inactivation of *Vibrio* spp. in seawater by SODIS (○), solar photocatalysis on hydrophilic surface (▲) and solar photocatalysis on hydrophobic surface (▲). The insert represent log-reduction obtained by adhesion of *Vibrio* spp. to coatings in darkness during experimental time. Each experimental point represents a mean value with coefficient of variation less than 30%

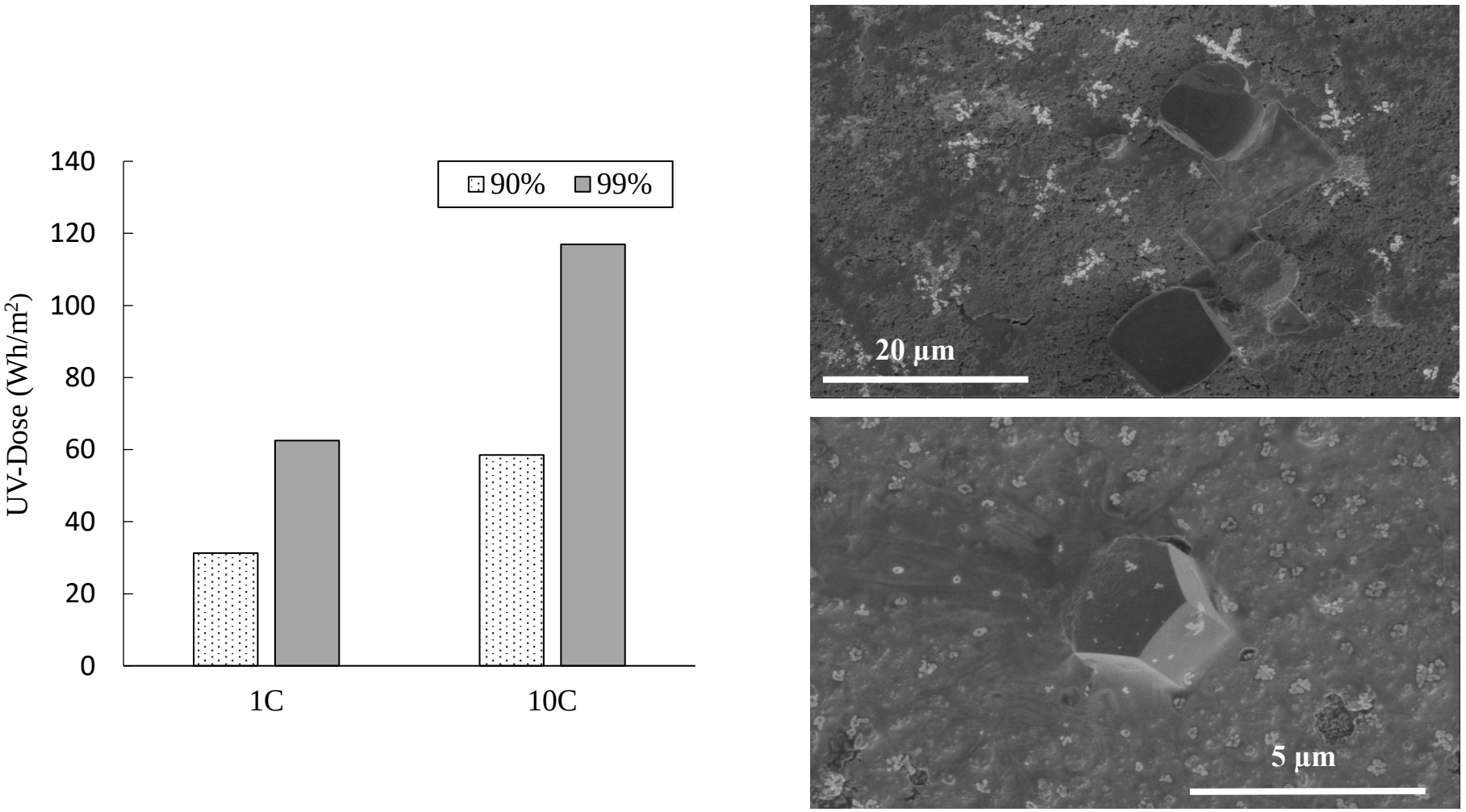


Figure 11. Left: Estimated UV-Dose required for reaching 90% and 99% inactivation of *Vibrio* spp. in seawater by solar photocatalysis on hydrophobic surface after 1 and 10 cycles (1C, 10C). **Right:** SEM images of the surface of hydrophilic (on the top) and hydrophobic (on the bottom) TiO_2/SiO_2 thin films after photocatalytic solar inactivation of *Vibrio* spp.