

ACS APPLIED ENERGY MATERIALS

Article

Rational Management of Photons for Enhanced Photocatalysis in Structurally-Colored Nanoporous Anodic Alumina Photonic Crystals

Siew Yee Lim, Cheryl Suwen Law, Marijana Markovic, Lluís F. Marsal, Nicolas H. Voelcker, Andrew D. Abell, and Abel Santos

ACS Appl. Energy Mater., **Just Accepted Manuscript** • DOI: 10.1021/acsaem.8b01721 • Publication Date (Web): 08 Jan 2019

Downloaded from <http://pubs.acs.org> on January 12, 2019

Just Accepted

“Just Accepted” manuscripts have been peer-reviewed and accepted for publication. They are posted online prior to technical editing, formatting for publication and author proofing. The American Chemical Society provides “Just Accepted” as a service to the research community to expedite the dissemination of scientific material as soon as possible after acceptance. “Just Accepted” manuscripts appear in full in PDF format accompanied by an HTML abstract. “Just Accepted” manuscripts have been fully peer reviewed, but should not be considered the official version of record. They are citable by the Digital Object Identifier (DOI®). “Just Accepted” is an optional service offered to authors. Therefore, the “Just Accepted” Web site may not include all articles that will be published in the journal. After a manuscript is technically edited and formatted, it will be removed from the “Just Accepted” Web site and published as an ASAP article. Note that technical editing may introduce minor changes to the manuscript text and/or graphics which could affect content, and all legal disclaimers and ethical guidelines that apply to the journal pertain. ACS cannot be held responsible for errors or consequences arising from the use of information contained in these “Just Accepted” manuscripts.



ACS Publications

is published by the American Chemical Society, 1155 Sixteenth Street N.W., Washington, DC 20036

Published by American Chemical Society. Copyright © American Chemical Society. However, no copyright claim is made to original U.S. Government works, or works produced by employees of any Commonwealth realm Crown government in the course of their duties.

Rational Management of Photons for Enhanced Photocatalysis in Structurally-Colored Nanoporous Anodic Alumina Photonic Crystals

*Siew Yee Lim^{1,2,3}, Cheryl Suwen Law^{1,2,3}, Marijana Markovic^{4,5}, Lluís F. Marsal^{*6},*

*Nicolas H. Voelcker^{*7,8,9,10}, Andrew D. Abell^{*2,3,11} and Abel Santos^{*1,2,3}*

¹School of Chemical Engineering, The University of Adelaide, Adelaide, South Australia 5005, Australia.

²Institute for Photonics and Advanced Sensing (IPAS), The University of Adelaide, Adelaide, South Australia 5005, Australia.

³ARC Centre of Excellence for Nanoscale BioPhotonics (CNBP), The University of Adelaide, Adelaide, South Australia 5005, Australia.

⁴School of Agriculture Food and Wine, The University of Adelaide, Adelaide, South Australia 5064, Australia.

⁵Center of Chemistry, Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Belgrade, Belgrade 11000, Serbia.

⁶Department of Electronic, Electric, and Automatics Engineering, Universitat Rovira i Virgili, Tarragona, Tarragona 43007, Spain.

⁷Melbourne Centre for Nanofabrication, Victorian Node of the Australian National Fabrication Facility, Monash University, Melbourne, Victoria 3168, Australia.

⁸Monash Institute of Pharmaceutical Sciences, Monash University, Melbourne, Victoria 3052, Australia.

⁹Commonwealth Scientific and Industrial Research Organisation (CSIRO), Melbourne, Victoria 3168, Australia.

¹⁰INM-Leibniz Institute for New Materials, Campus D2 2, Saarbrücken 66123, Germany.

¹¹Department of Chemistry, The University of Adelaide, Adelaide, South Australia 5005, Australia.

*E-mails: lluis.marsal@urv.cat ; nicolas.voelcker@monash.edu ;

andrew.abell@adelaide.edu.au ; abel.santos@adelaide.edu.au

KEYWORDS: Photocatalysis, Photonic Crystals, Slow Photons, Stopband, Pulse Anodization.

ABSTRACT: A comprehensive study on the engineering of titanium dioxide-functionalized nanoporous anodic alumina distributed Bragg reflectors (TiO₂-NAA-DBRs) for photocatalysis enhanced by the “slow photon” effect is presented. The photocatalytic performance of these composite photonic crystals (PCs) is assessed by monitoring photodegradation of a variety of organic molecules with absorbance bands across the spectral regions. This study demonstrates that photocatalytic performance of TiO₂-NAA-DBRs is enhanced by the “slow photon” effect when the edges of the PC’s photonic stopband (PSB) fall within the absorbance band of the organic molecules. The photocatalytic performance is significantly enhanced when the PSB’s red edge is in close proximity to the absorbance band of the organic molecules. Overall photocatalytic degradation is also dependent on the total pore length of the PC structure, charge of the organic molecules, percentage of vis-NIR irradiation and matrix complexity (i.e. interfering ions and molecules) when the PC’s PSB is partially or entirely misaligned with respect to the absorbance band of the organic molecules. Finally, the real-life application of TiO₂-NAA-DBRs to degrade pollutants such as pesticides in environmental matrices is

1
2
3 demonstrated. This study provides new insights into the development of rationally engineered,
4 high-performing, safe and reusable photocatalyst systems.
5

6 INTRODUCTION 7

8
9 Photonic crystals (PCs) are micro/nanostructures that play important roles in light-
10 driven applications, including photocatalysis¹⁻⁵, photovoltaics⁶⁻⁸, optics and biosensing⁹. The
11 rational design of the PC's structure amplifies light-matter interactions by controlling,
12 modulating, and trapping the propagation of electromagnetic waves across its structure *via*
13 Bragg diffraction, multiple scattering, and the "slow photon" effect.¹⁰⁻¹² Bragg diffraction
14 forbids light from propagating across the PC's structure due to its characteristic photonic
15 stopband (PSB). Multiple scattering reduces light loss due to reflection and increases the
16 optical path length of the flowing light at spectral regions that are away from the PC's PSB. As
17 a result, light is internally trapped within the PC, enhancing its light-confining properties.
18 Furthermore, photons propagate with strongly reduced group velocity ("slow photons") at the
19 frequency edges of the PC's PSB, giving rise to the so-called "slow photon" effect. Slow
20 photons are strongly localized in different dielectric parts of the PC's structure (i.e. sections of
21 high and low refractive index) at the edges of the PC's PSB (i.e. red and blue edges), enabling
22 a longer lifetime of photons at these spectral regions. This leads to an enhancement in the
23 overall optical absorbance of the material. Besides the enhanced light-matter interactions
24 attributed to the PC effect, nanoporous semiconductor PCs provide high specific surface area
25 that increases the number of functional sites available for reactions. The nanoporous structure
26 facilitates mass transport of ionic and molecular species involved in these photo-chemical
27 processes, and light harvesting capabilities for efficient management of photons at high-
28 irradiance spectral regions (i.e. visible and IR).^{1,4}
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53

54 Nanoporous semiconductor PC structures are superior to their nanoparticle-based
55 counterparts in light-driven applications. Particulate systems have a propensity to aggregate¹³
56 and are also difficult to be recovered after use¹⁴⁻¹⁵, becoming potentially toxic to the
57
58
59
60

1
2
3 environment¹⁶. Furthermore, most semiconductor nanoparticles only absorb light in the UV
4 region (i.e. ~ 5% of the solar spectrum) due to a high energy bandgap and the rapid
5 recombination of photogenerated charge carriers at their surface¹⁷⁻²⁰. These factors limit the
6 capability of nanoparticle-based systems to attain efficient and practical photon-to-electron
7 conversion rates for real-life light-driven processes. Films of nanoporous semiconductor PCs
8 can overcome these limitations due to their robust structure and unique set of physical and
9 chemical properties, which allows rational management of photons at the nanoscale to speed
10 up redox reactions. The advantages of photocatalyst semiconductor PC structures make them
11 desirable for a broad range of applications, including generation of hydrogen energy²¹⁻²⁴,
12 purification of air and water^{1-5,25}, production of chemicals such as ammonia (NH₃)²⁶, and
13 carbon dioxide (CO₂) reduction for environmental remediation²⁷⁻²⁸. Nanoporous
14 semiconductor PCs enable control of light-matter (i.e. photons-semiconductor) interactions at
15 the nanoscale in order to generate extra electron/hole (e⁻/h⁺) pairs and produce strongly
16 oxidizing and non-selective radicals for redox reactions.²⁹ Pure semiconductor PCs with
17 inverted opal structures have been widely employed for photocatalysis, particularly in water
18 purification.^{1,30-32} These semiconductor PC structures show enhanced performances in the
19 photodegradation of organic dye molecules under visible light irradiation when compared to
20 nanoparticle and non-porous film counterparts.

21
22 Photocatalytic enhancement in these systems is associated with the overall PC effect,
23 particularly with the “slow photon” effect when the edges of the PC’s PSB are tuned with
24 respect to the absorbance band of the organic dye or to the electronic bandgap of the material.
25 However, Zheng *et al.*¹ and Meng *et al.*³⁰ demonstrated that the performance of inverted opal
26 PC structures to degrade organic molecules can be inhibited when the absorbance band of these
27 molecules is located in the UV spectral region. These studies indicate that the photocatalytic
28 capability of these PC structures is limited to organic molecules with absorbance bands within
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 the visible spectral region under visible light irradiation. Furthermore, inverted opal PCs have
4
5 other intrinsic limitations, including limited versatility in tuning the PSB across the spectral
6
7 regions, restriction to 3D nanostructures, formation of structural defects (i.e. scattering
8
9 centers), limited to small domain areas, and require a long synthesis process (>24 h).^{4,33-36}
10
11 Significant effort has been devoted to developing alternative nanoporous semiconductor PC
12
13 structures capable of addressing these limitations to achieve enhanced performances for
14
15 photocatalysis. Amongst these, nanoporous PCs produced by electrochemical anodization of
16
17 valve metals have shown promising results in photocatalysis, including titanium dioxide
18
19 nanotubes³⁷⁻⁴⁰ and nanoporous anodic alumina (NAA)⁴. Anodization is an industrially scalable,
20
21 eco-friendly, highly-controllable, and low-cost electrochemical process broadly used in metal
22
23 finishing industry to modify the properties of metals such as color, brightness, wettability, and
24
25 corrosion protection. The generation of nanoporous PCs by anodization is a versatile approach
26
27 that enables the development of PC systems with precisely engineered optical properties for
28
29 different applications, including optical sensing and biosensing⁴¹⁻⁴⁴, light filtering⁴⁵⁻⁴⁶, energy
30
31 harvesting⁶⁻⁸, and photocatalysis^{4,37-40}. NAA produced by anodization of aluminum is an
32
33 excellent platform material to develop PC structures due to its highly versatile and controllable
34
35 nanoporous structure. However, NAA has a wide energy bandgap (i.e. 7.0–9.5 eV) that
36
37 prevents the direct use of NAA-PCs in photocatalysis. Despite this intrinsic limitation, we have
38
39 recently demonstrated that the chemical modification of NAA-PCs with layers of
40
41 semiconductor materials with narrower energy bandgap such as titanium dioxide (TiO₂ – 3.20–
42
43 3.35 eV) does enable the production of high-performing composite photocatalysts that
44
45 outperform conventional photocatalyst platforms.⁴ NAA-PCs have distinctive PSBs, the
46
47 features of which can be readily tuned across the spectral regions by engineering the effective
48
49 medium of NAA in a multi-dimensional fashion, through various anodization approaches.<sup>45,47-
50
51 52</sup> These NAA-PC platforms include optical microcavities^{47,48}, distributed Bragg reflectors
52
53
54
55
56
57
58
59
60

(DBR)^{45,49}, linear variable bandpass filters⁵⁰, gradient-index filters⁵¹, and hybrid PCs⁵². These PC structures provide new opportunities to rationally utilize the “slow photon” effect to attain an efficient management of photons at the nanoscale for photocatalytic applications.

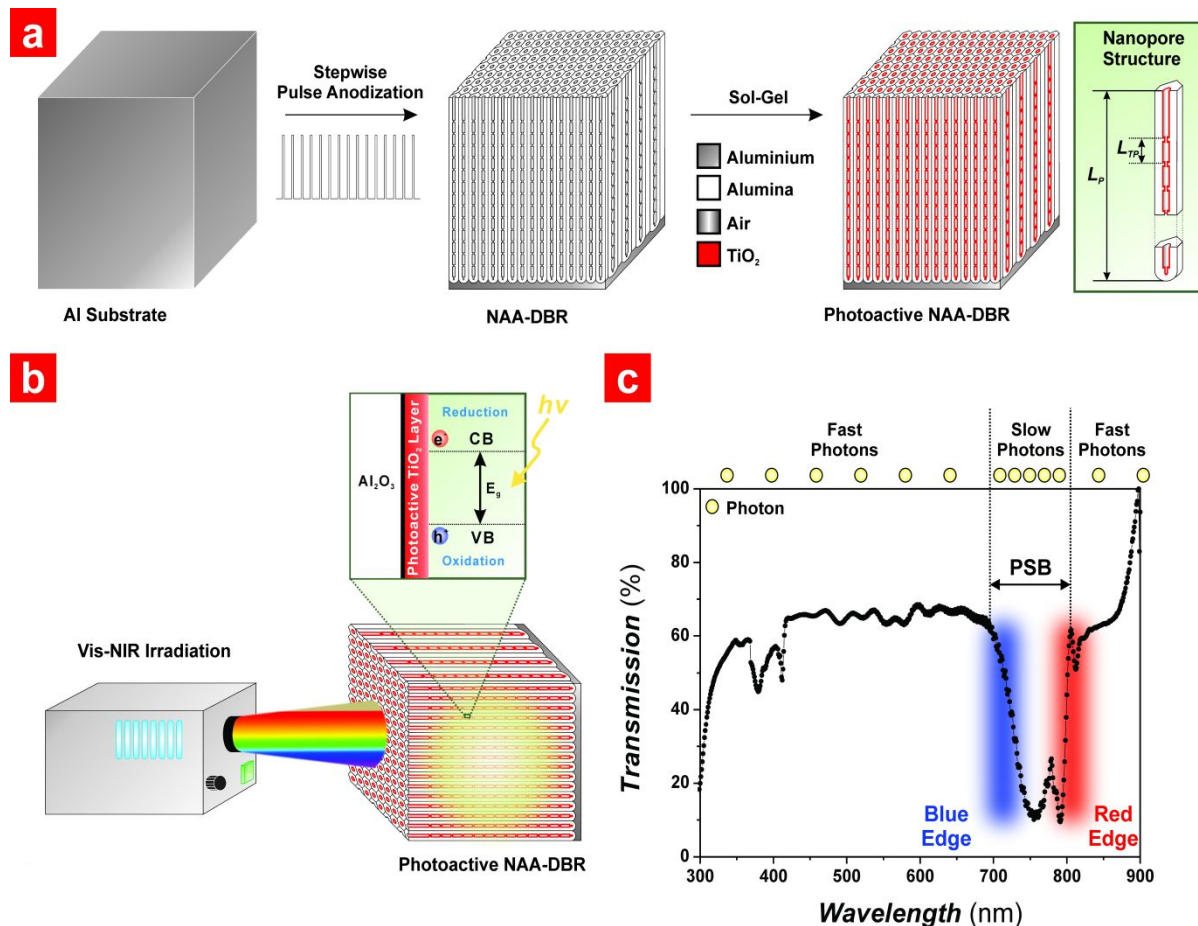


Figure 1. Fabrication and photocatalytic assessment of titania-functionalized structurally-colored nanoporous anodic alumina distributed Bragg reflectors (TiO₂-NAA-DBRs). a) Schematic illustrating the combination of stepwise pulse anodization (STPA) and sol-gel functionalization method used to fabricate TiO₂-NAA-DBRs with a visual description of the nanoporous structure of these photonic crystals (i.e. pore length – L_p and period length – L_{TP}). b) Schematic design of the photocatalytic assessment of TiO₂-NAA-DBRs under simulated visible-NIR irradiation conditions with details showing the chemical and electronic band structures of the composite photonic structures (note: E_g = energy band gap, $h\nu$ = excitation energy, CB = conduction, and VB = valence band). c) Representative transmission spectrum of a reference NAA-DBRs showing the effect of the photonic stopband (PSB) and its blue and red edges on the group velocity of photons across the spectral regions (note: NAA-DBR produced with anodization period – T_p = 1400 s, number of anodization pulses – N_p = 150 pulses, and pore widening time – t_{pw} = 0 min, where the medium filling the nanopores is water).

Herein, we develop and study photoactive TiO₂-functionalized structurally-colored NAA-DBRs as photoactive PC platforms for enhanced photocatalytic degradation of organic molecules. NAA-DBRs are fabricated by stepwise pulse anodization (STPA) and subsequently functionalized with photoactive layers of TiO₂ by sol-gel method (**Figure 1**). Photocatalytic

1
2
3 performance of TiO₂-NAA-DBRs is assessed under controlled visible-NIR irradiation
4
5 conditions by a systematic modification of several parameters, including the anodization period
6
7 (i.e. features of PSB), concentration of hydrogen peroxide, characteristics of model organic
8
9 molecules, and complexity of liquid matrix. This approach enables the identification of
10
11 photocatalytic enhancements by the “slow photon” effect, using TiO₂-NAA-DBRs as model
12
13 photocatalyst platforms under controlled irradiation conditions. Furthermore, other critical
14
15 factors for real-life applications such as reusability and photodegradation of model pesticides
16
17 by TiO₂-NAA-DBRs are demonstrated.
18
19
20

21 22 EXPERIMENTAL SECTION 23

24 **2.1. Materials.** High purity (99.9997%) aluminum (Al) foils 0.32 mm thick were purchased
25
26 from Goodfellow Cambridge Ltd. (UK). Hydrochloric acid (HCl), copper (II) chloride (CuCl₂),
27
28 perchloric acid (HClO₄), sodium chloride (NaCl), titanium (IV) butoxide (Ti(OBu)₄), hydrogen
29
30 peroxide (H₂O₂), methyl orange (MO), methylene blue (MB), rhodamine B (RhoB), and 4-
31
32 chlorophenol (4-CP) were supplied by Sigma-Aldrich (Australia). Ethanol (EtOH – C₂H₅OH)
33
34 and sulfuric acid (H₂SO₄) were purchased from ChemSupply (Australia). Ultrapure Milli-Q®
35
36 water (18.2 MΩ cm) was used in the preparation of all the aqueous solutions used in this study.
37
38
39

40
41 **2.2. Fabrication of NAA-DBRs.** NAA-DBRs were produced by stepwise pulse anodization
42
43 (STPA) under current density control conditions.⁴⁹ Prior to anodization, 1.5 x 1.5 cm² square
44
45 chips were sonicated in ethanol and water for 15 min each, dried under air stream and
46
47 electropolished in a mixture of EtOH and HClO₄ 4:1 (v:v) at 20 V and 5 °C for 3 min. The
48
49 electropolished Al chips were anodized in an aqueous solution of 1.1 M H₂SO₄ with 25 v% of
50
51 EtOH at 1 °C. The anodization process started with a constant current density of 1.120 mA cm⁻²
52
53 for 1 h to achieve a homogeneous pore growth rate prior to stepwise pulse anodization. The
54
55 anodization profile was subsequently switched to stepwise pulse mode, where the current
56
57 density was pulsed between high ($J_{max} = 1.120 \text{ mA cm}^{-2}$) and low ($J_{min} = 0.280 \text{ mA cm}^{-2}$) current
58
59
60

density values following a stepwise modulation for a total of 150 anodization pulses (N_P). The anodization period (T_P) (i.e. time between consecutive pulses) was modified from 900 to 1600 s with an interval (ΔT_P) of 100 s. Note that T_P is given by **Equation 1**:

$$T_P = t_{max} + t_{min} \quad (1)$$

where t_{max} and t_{min} are the time for maximum and minimum current density pulses (i.e. $J_{max} = 1.120 \text{ mA cm}^{-2}$ and $J_{min} = 0.280 \text{ mA cm}^{-2}$), respectively, and the time ratio for t_{max} and t_{min} ($t_{max}:t_{min}$) was set to 1:4 for $T_P = 900$ to 1600 s.

2.3. Surface Functionalization of NAA-DBRs with Photoactive Layers of TiO₂. The inner surface of NAA-DBRs was chemically functionalized with TiO₂ photoactive layers through the sol-gel method. The TiO₂ sol was prepared by magnetically stirring a mixture of titanium (IV) butoxide (3 v%) and EtOH (97 v%) for 10 min. NAA-DBRs were subsequently soaked in the TiO₂ sol for 24 h. The surface-functionalized NAA-DBRs were washed with EtOH to remove any excess of TiO₂ sol and titanium (IV) butoxide. The TiO₂-NAA-DBRs were then dried in an oven at 50 °C for 10 min to evaporate any remaining EtOH residues.

2.4. Optical Characterization. Prior to transmission spectra acquisition, NAA-DBRs were chemically etched in a saturated solution of HCl/CuCl₂ using a 5 mm diameter circular window etching mask to selectively dissolve the underlying Al substrate at the backside. Transmission spectra of chemically etched NAA-DBRs fabricated with different anodization periods were obtained in air and water from 200 to 800 nm at normal incidence (i.e. $\theta = 0^\circ$), using a UV-visible spectrophotometer (Cary 300, Agilent, USA). The absorbance spectra of 5 mg L⁻¹ organics (i.e. MO, RhoB, MB, and 4-CP) in a quartz cuvette of 10 mm path length were acquired from 200 to 800 nm to determine the absorbance bands of the organics. The interferometric color of NAA-DBRs in air and water was characterized by digital pictures,

1
2
3 using a Canon EOS 700D digital camera equipped with a Tamron 90 mm F2.8 VC USD macro
4 mount lens with autofocus function under natural light illumination.
5
6

7 8 **2.5. Photocatalytic Degradation of Organics under Controlled Irradiation Conditions.**

9
10 Photocatalytic performance of TiO₂-NAA-DBRs fabricated with various T_P was assessed under
11 simulated solar light irradiation conditions, using the degradation of a model organic dye,
12 methylene blue (MB), with well-defined absorbance band within the visible spectral range (i.e.
13 MB – $\lambda_{Abs-MB} = 664$ nm) as an efficiency indicator. A 2 mL mixture of 5 mg L⁻¹ of MB and 100
14 mM H₂O₂ solution was pipetted into a transparent cuvette. The TiO₂-NAA-DBRs, which had
15 an effective area of 1 cm², were then submerged inside the organic mixture. The solution was
16 magnetically stirred in a dark vessel (i.e. solar simulator) for 30 min to achieve the adsorption-
17 desorption equilibrium prior to irradiation. The system was subsequently illuminated with
18 simulated solar light irradiation using a 150 W (~3000 lumen) halogen lamp (HL250-A,
19 Amscope, Australia) at room temperature. To determine the concentration of MB at specific
20 time intervals, the absorbance of the MB solution at $\lambda_{Abs-MB} = 664$ nm for each illumination
21 time interval (i.e. 15 min) was analyzed by UV-visible spectroscopy. The relationship between
22 the absorbance intensity and the concentration of MB was established by a calibration line to
23 obtain the photocatalytic conversion ratio (C_t/C_o), where C_o is the concentration of organic after
24 stirring in the dark for 30 min and C_t is the concentration at illumination time t (**Figure S1 –**
25 **Supporting Information**). This parameter was used in determining the kinetic model for this
26 photocatalytic system. The effect of the type of organic dye and the concentration of H₂O₂ on
27 the photocatalytic performance of TiO₂-NAA-DBRs fabricated with $T_P = 1200$ s was
28 systematically assessed by modifying the organic molecule model (i.e. MB, MO, and RhoB;
29 MO – $\lambda_{Abs-MO} = 464$ nm and RhoB – $\lambda_{Abs-RhoB} = 554$ nm) and the concentration of H₂O₂ solution
30 (i.e. 12.5, 50.0, 100, and 200 mM), respectively. The reusability of TiO₂-NAA-DBRs
31 fabricated with $T_P = 1200$ s was assessed under simulated solar light irradiation by repeating
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 the photocatalytic degradation of MB molecules five times using the same photocatalyst
4 platform. The TiO₂-NAA-DBR was washed in EtOH and water under sonication for 15 min
5 each and dried under air stream before each photocatalytic cycle. To demonstrate the
6 photocatalytic capability of TiO₂-NAA-DBRs for real-life applications, the photodegradation
7 of 4-CP (i.e. $\lambda_{Abs-4-CP} = 225$ nm), a model pesticide, by TiO₂-NAA-DBRs was investigated.
8 Two main parameters were assessed: i) the effect of the anodization period (i.e. $T_p = 900, 1200,$
9 and 1600 s) and ii) the composition of the aqueous matrix of 4-CP (i.e. milli-Q water, tap water,
10 filtered Torrens river water, and 10 g L⁻¹ NaCl aqueous solution).
11
12
13
14
15
16
17
18
19
20
21
22

23 **2.6. Chemical and Structural Characterization.** The structural features of NAA-DBRs were
24 characterized using a field emission gun scanning electron microscope (FEG-SEM FEI Quanta
25 450). FEG-SEM images were analyzed by ImageJ.⁵⁴ The chemical composition of NAA-DBRs
26 before and after surface functionalization with TiO₂ was analyzed by energy dispersive X-ray
27 (EDX) spectroscopy during FEG-SEM characterization.
28
29
30
31
32
33
34

35 RESULTS AND DISCUSSION

36
37 **3.1. Fabrication and Structural Characterization of NAA-DBRs.** **Figure 2** shows a
38 representative STPA profile with a graphical description of the different anodization
39 parameters and a set of representative FEG-SEM images of NAA-DBRs produced by STPA
40 process. The anodization profile reveals that the anodization voltage (i.e. output) follows
41 closely the anodization current density (i.e. input) applied during the STPA process. Thus, the
42 anodization conditions used in our study enable the efficient translation of the anodization
43 current density profiles into changes in the porosity of NAA in depth (**Figure 2a**). The
44 anodization process begins with a constant current anodization step (CA) (**Figure 2b**), which
45 produces a layer of NAA with straight nanopores. This process is followed by the STPA stage,
46 during which stacked layers of NAA with stepwise porosity are generated, as depicted in the
47 FEG-SEM image shown in **Figure 2c**. A top view FEG-SEM image reveals that the nanopores
48
49
50
51
52
53
54
55
56
57
58
59
60

are evenly and randomly distributed across the surface of NAA-DBRs, with an average nanopore diameter (d_p) measured to be 10 ± 3 nm (Figure 2d).

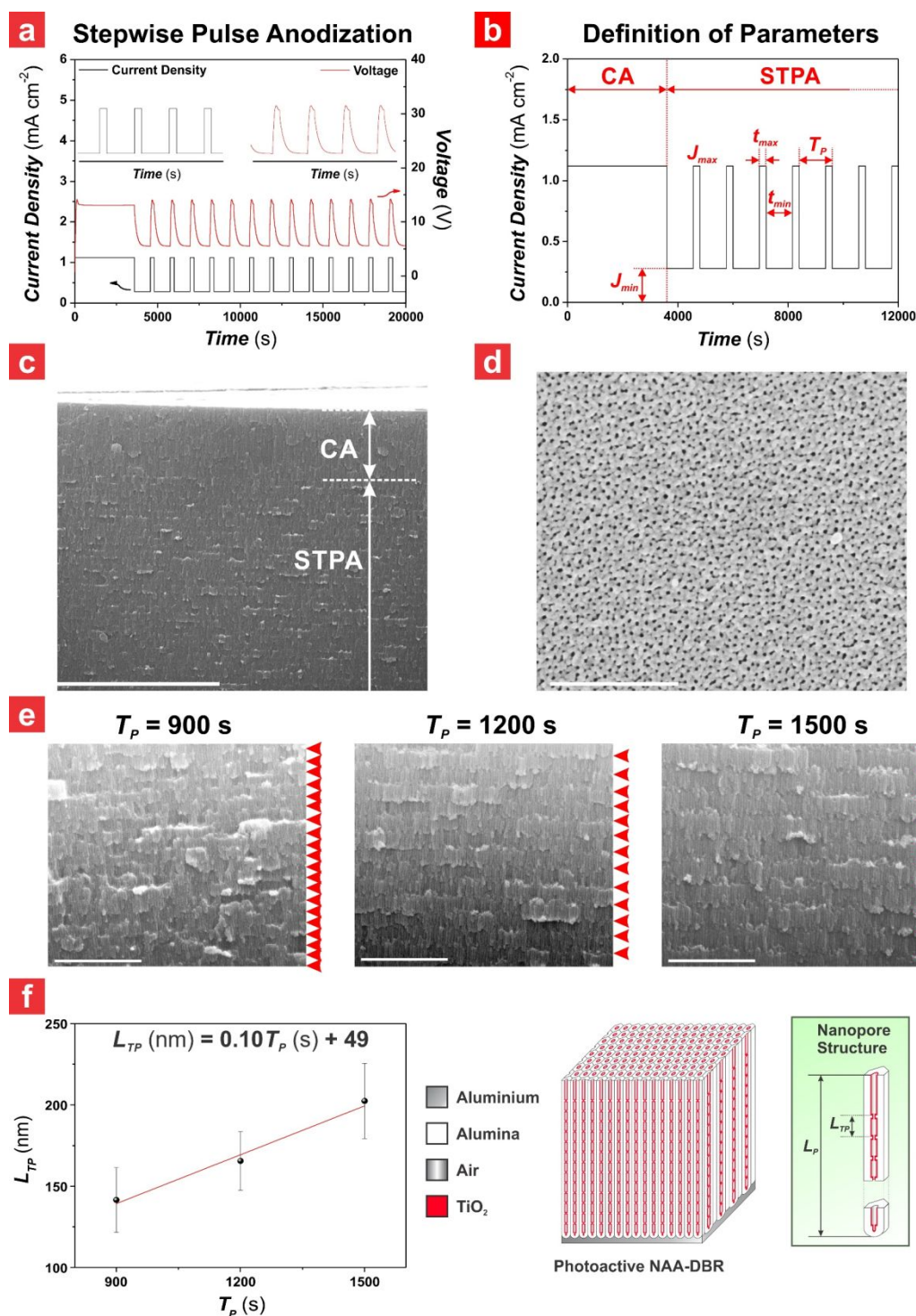


Figure 2. Fabrication and structural characterization of the nanoporous structure of NAA-DBRs fabricated by stepwise pulse anodization (STPA). a) Representative anodization profile used to produce NAA-DBRs with and anodization period (T_p) of 1200 s and 150 anodization pulses (N_p) by STPA approach. b) Graphical definition of the anodization parameters (i.e. J_{min} , J_{max} , t_{min} , t_{max} , and T_p) used to generate the STPA profiles (note: CA = constant current anodization step). c) General cross-sectional FEG-SEM image view of a NAA-DBR (scale bar = 4 μ m).

1
2
3 d) Top view FEG-SEM image of a NAA-DBR fabricated with $T_p = 900$ s and $N_p = 150$ pulses (scale bar = 500
4 nm). e) FEG-SEM images showing cross-sectional views of NAA-DBRs fabricated with $T_p = 900$ s (left), $T_p =$
5 1200 s (center) and $T_p = 1500$ s (right) (scale bar = 1 μm) (note: red arrowheads denote the interfaces between
6 anodization periods, L_{TP}). f) Linear correlation between L_{TP} and T_p (left) with schematic description of L_{TP} in the
7 nanoporous photonic crystal structure (right) (note: error bars denote standard deviation from average
8 measurements obtained from $n = 3$ independent NAA-DBRs).
9

10 A visual analysis of NAA-DBRs fabricated with different anodization period (i.e. $T_p = 900,$
11 1200, and 1600 s) demonstrates that the period length (L_{TP}) of the stacked layers of NAA
12 (graphic illustration in **Figure 1a**), as indicated by the red arrowheads shown in the cross-
13 sectional FEG-SEM images shown in **Figure 2e**, increases with T_p . The correlation between
14 L_{TP} and T_p follows a linear relationship, where L_{TP} increases at a rate of 0.10 nm s⁻¹ with
15 increasing T_p (**Figure 2f**).
16
17
18
19
20
21
22
23

24 **3.2. Effect of Anodization Period and Surface Functionalization on the Optical Properties**

25 **of NAA-DBRs.** **Figure 3** depicts the dependence of the optical properties of NAA-DBRs on
26 the anodization period (T_p) in air and water as well as the chemical composition analysis of the
27 NAA-DBRs before and after surface functionalization with photoactive layers of TiO₂. The
28 combined effect of T_p and media filling the nanoporous network of NAA-DBRs on the position
29 of the characteristic photonic stopband (PSB) were systematically studied by modifying T_p
30 from 900 to 1600 s with $\Delta T_p = 100$ s in air and water (H₂O) (**Figure 3a**). It is noteworthy that
31 the photocatalytic reactions assessed in our study were performed in aqueous media. Therefore,
32 establishing the photonic characteristics of NAA-DBRs in water is critical to understand the
33 system's performance and identify photocatalytic performance enhancements associated with
34 the "slow photon" effect. An analysis of the correlation between T_p and the central wavelength
35 (λ_c) of the characteristic PSB establishes a linear relationship between these two parameters in
36 both air and H₂O, with slopes 0.34 ± 0.03 and 0.44 ± 0.04 nm s⁻¹, respectively. In air, the
37 position of the PSB can be tuned from 492 ± 1 to 740 ± 1 nm on varying T_p from 900 to 1600
38 s. This demonstrates that the position of characteristic PSB red shifts with T_p . This result is
39 further supported by the interferometric color displayed by these NAA-PCs, as indicated by
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 the digital images shown in **Figure 3a**, and the transmission spectra of NAA-DBRs shown in
4
5 **Figure S2 (Supporting Information)**. Structurally-colored NAA-DBRs display vivid colors
6
7 in air, varying from purple ($T_P = 900$ s), periwinkle ($T_P = 1000$ s), blue ($T_P = 1100$ s), green
8
9 ($T_P = 1200$ s), yellow ($T_P = 1300$ s), chartreuse ($T_P = 1400$ s), orange ($T_P = 1500$ s) to light
10
11 brown ($T_P = 1600$ s). This phenomenon is attributable to a more efficient reflection of light by
12
13 the PC structure at those spectral regions where the PSB is located.⁴⁹ Similarly, the position of
14
15 the characteristic PSB also red-shifts from 521 ± 1 to 839 ± 2 nm with T_P from 900 to 1600 s
16
17 when the nanopores of NAA-DBRs are infiltrated with H₂O. The position of the characteristic
18
19 PSB is red-shifted at an average rate of 65 ± 26 nm s⁻¹ on changing the media within the
20
21 nanoporous network of NAA-DBRs from air to H₂O. This red-shift is due to the infiltration of
22
23 nanopores with a medium of higher refractive index than that of air (i.e. $n_{\text{air}} = 1.00$ RIU and
24
25 $n_{\text{H}_2\text{O}} = 1.33$ RIU).

26
27
28 **Figure 3b** compiles a set of digital pictures of NAA-DBRs partially covered with transparent
29
30 tape displaying interferometric colors as a function of T_P and the media infiltrating the
31
32 nanopores (i.e. air and water). The left part of the photo in each digital image corresponds to
33
34 the interferometric color displayed by NAA-DBRs in air while the right part corresponds to
35
36 that in H₂O. As commented above, NAA-DBRs display vivid interferometric colors in air (i.e.
37
38 purple – $T_P = 900$ s, periwinkle – $T_P = 1000$ s, blue – $T_P = 1100$ s, green – $T_P = 1200$ s, yellow
39
40 – $T_P = 1300$ s, chartreuse – $T_P = 1400$ s, orange – $T_P = 1500$ s, and light brown – $T_P = 1600$ s),
41
42 which red-shift with T_P . Similarly, the interferometric color also red-shifts with T_P when the
43
44 nanopores of NAA-DBRs are filled with H₂O. Furthermore, these images indicate that, when
45
46 the nanopores are filled with H₂O, the interferometric color is also red-shifted for all T_P , except
47
48 for $T_P = 1600$ s, which displays light brown interferometric color at both parts of the digital
49
50 picture. Note that the interferometric color relies upon the position of the characteristic PSB
51
52 within UV-visible-NIR spectrum. As such, NAA-DBRs featuring the characteristic PSB within
53
54
55
56
57
58
59
60

the visible spectrum display interferometric color, from purple to orange, while those NAA-DBRs with PSB in the NIR spectral range are light brown, which is the characteristic color of NAA produced under the fabrication conditions used in this study.

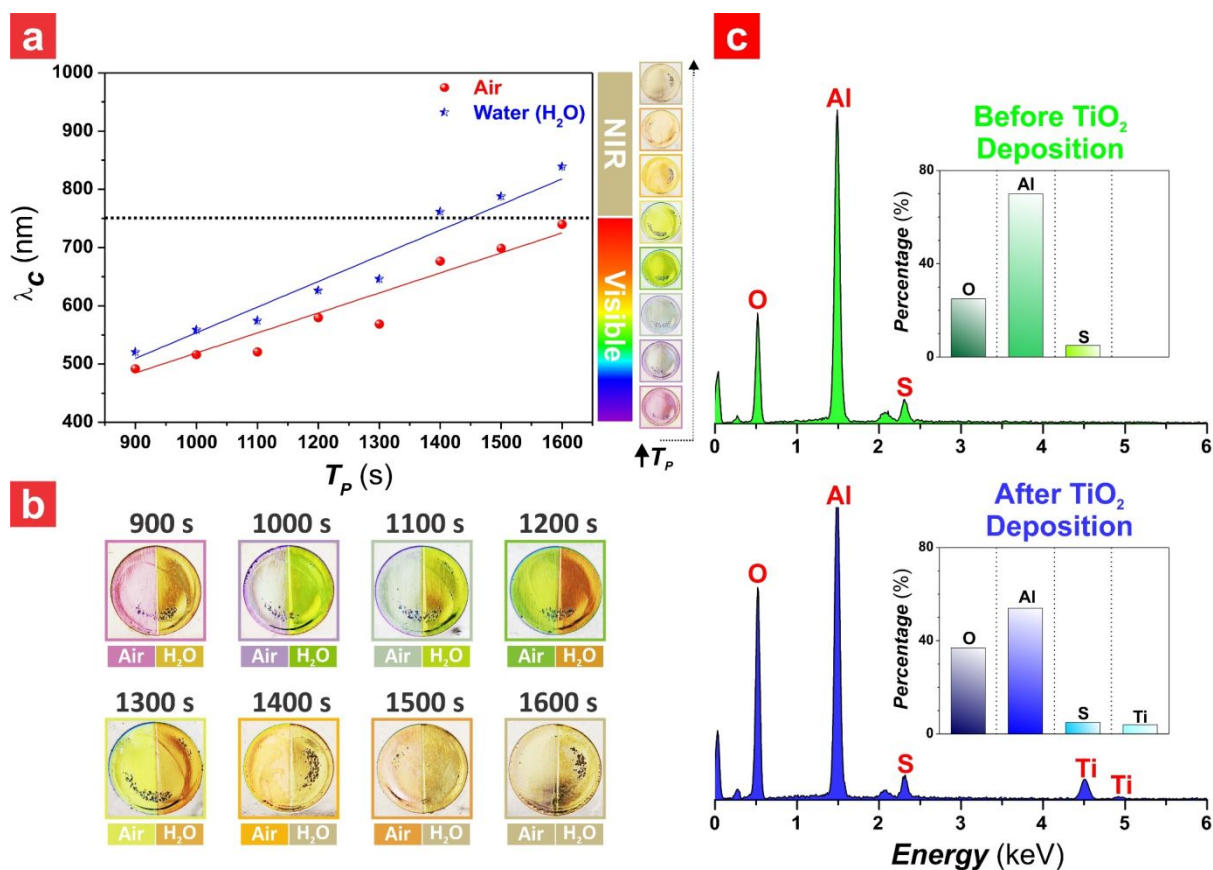


Figure 3. Optical tunability of the PSB of NAA-DBRs by varying anodization period (T_p) and chemical analysis of the composite photonic structures after surface functionalization with photoactive layers of TiO_2 . a) Position of the characteristic photonic stopband (PSB - λ_c) as a function of media (left) and digital images displaying the interferometric color of NAA-DBRs from $T_p = 900$ to 1600 s with $\Delta T_p = 100$ s in air (right) (note: error bars correspond to standard deviation from $n = 3$ independent measurements). b) Interferometric color of NAA-DBRs as a function of T_p and media (note: sample diameter 1 cm). c) Energy dispersive X-ray (EDX) spectra of a representative NAA-DBR with insets showing the percentage of main elements present before and after surface functionalization with TiO_2 (note: NAA-DBR produced with $T_p = 1200$ s and $N_p = 150$ pulses).

The inner surface of NAA-DBRs was coated with photoactive layers of TiO_2 by means of the sol-gel method. **Figure 3c** shows the energy dispersive X-ray (EDX) spectra with insets depicting the percentage of the elements present in as-produced (before sol-gel deposition) and TiO_2 -functionalized (after sol-gel deposition) NAA-DBRs. The EDX spectra reveal that while the intensity of Al and S atoms are constant after the functional TiO_2 layers are deposited onto the NAA-DBRs, the intensity of O and Ti atoms increases. For instance, the relative percentage

1
2
3 of O, Al, S and Ti atoms in as-produced NAA-DBRs was 25, 70, 5, and 0%, respectively. Note
4 that for this EDX spectrum, Al and O atoms correspond to alumina (Al_2O_3) while S atoms were
5 incorporated into the structure of NAA from the acid electrolyte during anodization. After
6 chemical modification of NAA-DBRs with TiO_2 , the relative percentage of O, Al, S and Ti
7 atoms were determined to be 37, 54, 5, and 4%, respectively. This analysis demonstrates the
8 successful deposition of TiO_2 layers onto the inner surface of NAA-DBRs. The
9 crystallographic phase of the TiO_2 layers under the synthesis conditions used in our study was
10 amorphous (**Figure S3 – Supporting Information**).⁴

11
12 To summarize, modification of the anodization period can be used to precisely tune the optical
13 properties (i.e. position of the PSB and interferometric color) of NAA-DBRs across the entire
14 visible-NIR spectrum. Furthermore, the inner surface of NAA-DBRs can be functionalized
15 with photoactive layers of TiO_2 through sol-gel method to create composite semiconductor PC
16 structures for photocatalysis.

17
18 **3.3. Assessment of Photocatalytic Degradation of Model Organic Molecules by TiO_2 -**
19 **NAA-DBRs.** The photocatalytic performance of TiO_2 -NAA-DBRs produced with varied T_P
20 (i.e. from 900 to 1600 s with $\Delta T_P = 100$ s) was assessed by investigating the photocatalytic
21 degradation of three model pollutants (i.e. methyl orange – MO, rhodamine B – RhoB, and
22 methylene blue – MB) under simulated solar light irradiation. **Figure S4 (Supporting**
23 **Information)** displays the absorbance spectra of these organic molecules with the
24 corresponding absorbance bands at 464, 554, and 664 nm, respectively. **Figure S5**
25 **(Supporting Information)** illustrates the simulated solar spectrum used in this study. Analysis
26 of this spectrum reveals a spectral distribution of 0.12% UV (350–400 nm), 64.60% visible
27 (400–750 nm) and 35.28% NIR (800–1025 nm). The photocatalytic reactions performed in this
28 study are thus driven by visible-NIR light irradiation (i.e. 400–1025 nm), which is far from the
29 characteristic energy bandgap of TiO_2 (i.e. 3.20–3.35 eV = 370–387 nm). Note that 100 mM
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

of H₂O₂ was added to the reaction solution to aid the photogeneration of charge carriers (e⁻/h⁺) in the photoactive TiO₂ layers deposited onto the inner surface of NAA-DBRs. The concentration of organic molecules with time in the reaction solution during the photo-driven degradation process (C_t) was estimated from the calibration lines shown in **Figure S1**. The photocatalytic performance of TiO₂-NAA-DBRs was fitted and calculated through the linearized pseudo-first order kinetics model shown in **Equation 2**:

$$-\ln(C_t/C_o) = kt \quad (2)$$

where C_o is the concentration after stirring in the dark for 30 min, C_t is the concentration at illumination time t , and k is the characteristic kinetic constant.

3.4. Effect of Anodization Period on Photocatalytic Degradation of MB. “Slow photons” are photons with reduced group velocity near the vicinity of the PSB of PCs. This effect increases the overall absorbance of the PC material, enhancing light–matter interactions for light harvesting since photons spend longer time within the photocatalytic material (i.e. generation of extra e⁻/h⁺ pairs for photocatalysis).^{12,54} The well-defined and spectrally controllable PSB of TiO₂-NAA-DBRs make these PC structures excellent candidates to study and utilize these light-matter interactions at the nanoscale. Photocatalytic degradation of MB under simulated sunlight irradiation conditions was used as a model reaction to identify “slow photon” effects in TiO₂-NAA-DBRs fabricated with varying T_P from 900 to 1600 s, with $\Delta T_P = 100$ s. **Figures 4a and b** and **Table 1** show the effect of T_P as a function of the relative position of the edges of the PSB of TiO₂-NAA-DBRs and the absorbance band of MB, using its photocatalytic degradation under simulated solar light irradiation as an indicator of “slow photon” enhancements. The kinetic constant (k) for TiO₂-NAA-DBRs with $T_P = 900, 1000, 1100, 1200, 1300, 1400, 1500,$ and 1600 s were $1.83 \pm 0.01, 2.00 \pm 0.06, 2.80 \pm 0.04, 3.04 \pm 0.01, 2.63 \pm 0.10, 2.22 \pm 0.09, 2.77 \pm 0.15,$ and 2.37 ± 0.08 h⁻¹, respectively (**Figure 4a** and **Table 1**). The highest k value was achieved by TiO₂-NAA-DBRs produced with $T_P = 1200$ s,

1
2
3 indicating that these composite semiconductor PCs provide the fastest and most efficient
4 platform to photodegrade MB, with a 8–40% superior performance than that achieved by their
5 counterparts produced with shorter or longer T_p . **Figure 4b** and **Table 1** indicate that the
6 position of the red edge of the PSB of TiO₂-NAA-DBRs fabricated with $T_p = 1200$ s is the
7 closest to the absorbance band of MB (i.e. $\lambda_{Abs-MB} = 664$ nm) (i.e. ~17 nm away from the
8 absorbance band maximum of MB). Upon irradiation, slow photons are strongly localized in
9 the high (i.e. photoactive layer of TiO₂) and low (i.e. organic solution) dielectric parts of the
10 red and blue edges of the characteristic PSB, respectively.⁵⁴ This phenomenon results in a
11 longer lifetime of photons that increases the effective optical path length of the light waves
12 when photons travel across the TiO₂-NAA-DBRs' structure. This enhanced light–matter
13 interaction promotes the photon-to-electron conversion rate in these composite PC structures,
14 speeding up the photocatalytic degradation of MB significantly when the edges of the PSB are
15 located close to the absorbance band maximum of MB.⁵⁴⁻⁵⁶ The “slow photon” effect is even
16 more apparent when the red edge of the PSB is in the proximity of the absorbance band of MB.
17 Here slow photons in that spectral region are strongly localized in the high refractive index
18 region of the PC (i.e. semiconductor – TiO₂).^{12,54} Our results confirm this hypothesis since this
19 model photodegradation reaction is enhanced when the red edge of the PSB of TiO₂-NAA-
20 DBRs is at its closest to the absorbance band maximum of MB.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44

45 The red edge of the PSB of TiO₂-NAA-DBRs produced with $T_p = 1100$ s is the second closest
46 to the absorbance band maximum of MB (i.e. ~26 nm away). These PC structures are the
47 second best performing type of TiO₂-NAA-DBR (i.e. $k = 2.80 \pm 0.04$ h⁻¹). This further confirms
48 the hypothesis that the relative position of the red edge of the PSB with respect to the
49 absorbance band of the organic model molecule plays a more significant role than that of the
50 blue edge in enhancing the photocatalytic degradation of MB through “slow photon” effect.
51
52
53
54
55
56
57
58
59 Although the red edge of the PSB of TiO₂-NAA-DBRs produced with $T_p = 1300$ s is the third
60

1
2
3 closest to the absorbance band maximum of MB (i.e. ~ 49 nm away), these PC platforms are
4 slightly outperformed by TiO₂-NAA-DBRs fabricated with $T_P = 1500$ s, which achieve
5 approximately 5% superior performance. **Figure 4b** shows that the characteristic PSB of TiO₂-
6 NAA-DBRs produced with $T_P = 1500$ s partially overlaps with the absorbance band of MB,
7 where the blue edge is 55 nm removed from the absorbance band maximum of MB. The red
8 edge of the PSB of these PCs falls completely outside of the absorbance band. Since the blue
9 edge of the PSB of these TiO₂-NAA-DBRs is located inside the absorbance band of MB, a
10 partial enhancement of the photocatalytic performance due to “slow photon” effect is expected.
11 However, since the PSB is practically located outside of the absorbance range of MB,
12 photocatalytic enhancement under such a configuration relies strongly on other factors such as
13 the geometric features of the overall PC structure. As indicated in **Table 1**, TiO₂-NAA-DBRs
14 fabricated with $T_P = 1500$ s are produced with the second longest anodization time (i.e. $t_{An} =$
15 63.5 h), which is calculated from the number of anodization pulses ($N_P = 150$ pulses) and the
16 anodization period ($T_P = 1500$ s) by **Equation 3**:

$$t_{An} = N_P/T_P \quad (3)$$

17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40 The total thicknesses or pore length (L_P – **Figure 1a**) of TiO₂-NAA-DBRs is directly
41 proportional to the anodization time. An increase in total thicknesses of the PC platform
42 enhances its overall light absorption, since more semiconductor matter is available for light-
43 matter interactions.^{41,57} This leads to the photogeneration of extra charge carriers (e^-/h^+) and
44 thus to an enhancement of the photocatalytic activities achieved by those TiO₂-NAA-DBRs
45 featuring thicker structure. The unexpectedly higher performance shown by TiO₂-NAA-DBRs
46 produced with $T_P = 1500$ s is thus attributed to two contributing factors, a partial alignment of
47 the blue edge of the PSB with respect to the absorbance band of MB and the total thickness of
48 the PC platform. The fifth best performing TiO₂-NAA-DBRs platforms are those produced
49 with $T_P = 1600$ s. These semiconductor PCs feature a PSB located almost entirely outside of
50
51
52
53
54
55
56
57
58
59
60

1
2
3 the absorbance range of MB. Despite having the longest t_{An} (i.e. 67.7 h), the photocatalytic
4 performance shown by these TiO₂-NAA-DBRs is less efficient than that achieved by TiO₂-
5 NAA-DBRs fabricated with $T_p = 1500$ s by ~14%. This result is attributable to the negligible
6 contribution by “slow photon” effect to the photocatalytic performance since the blue edge of
7 the PSB of these PCs is very far away from the absorbance band of MB (i.e. ~74 nm).

8
9
10
11
12
13
14 The blue edge of the PSB of TiO₂-NAA-DBRs fabricated with $T_p = 1400$ s is relatively close
15 to the absorbance band maximum of MB (i.e. ~55 nm). However, these composite photonic
16 structures provide the sixth best performance in degrading the model organic molecule (i.e. k
17 = 2.22 ± 0.09 h⁻¹). TiO₂-NAA-DBRs produced with $T_p = 1400$ s feature a thinner structure (i.e.
18 $t_{An} = 59.3$ h) than that of those TiO₂-NAA-DBRs produced with $T_p = 1500$ and 1600 s (i.e. t_{An}
19 = 63.5 and 67.7 h, respectively). This result is attributable to an inefficient combination of both
20 “slow photon” effect and overall thickness of the PC structure, with a partial alignment of the
21 PSB’s blue edge and shorter pore length in the PC structure. The worst performing TiO₂-NAA-
22 DBR structures have a $T_p = 900$ and 1000 s, with degradation rates $k = 2.00 \pm 0.06$ and $1.83 \pm$
23 0.01 h⁻¹, respectively. TiO₂-NAA-DBRs produced with $T_p = 900$ and 1000 s feature PSBs that
24 are partially and entirely located within the absorbance range of MB, respectively. However,
25 the red edge of the PSBs of these PCs is removed from the absorbance band maximum of MB
26 (i.e. ~52 and 103 nm). Furthermore, these PCs have the thinnest structures (i.e. $t_{An} = 38.5$ and
27 42.7 h, respectively). Thus, a combination of a relative misalignment between the PSB’s red
28 edge and the thinnest PC structure has a significant detrimental effect on the overall
29 photodegradation performance of these semiconductor PCs. This analysis establishes that the
30 photocatalytic performance of TiO₂-NAA-DBRs with various T_p follows the order $1200 > 1100$
31 $> 1500 > 1300 > 1600 > 1400 > 1000 > 900$ s. Changes in the characteristic color of the MB
32 solution upon degradation by TiO₂-NAA-DBRs under simulated irradiation conditions, from 0
33 to 60 min with an interval of 15 min (**Figure S6 – Supporting Information**) also confirm the
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

photocatalytic degradation efficiency of TiO₂-NAA-DBRs by visual analysis. This result further demonstrates that MB molecules are efficiently photodegraded by TiO₂-NAA-DBRs after 1 h.

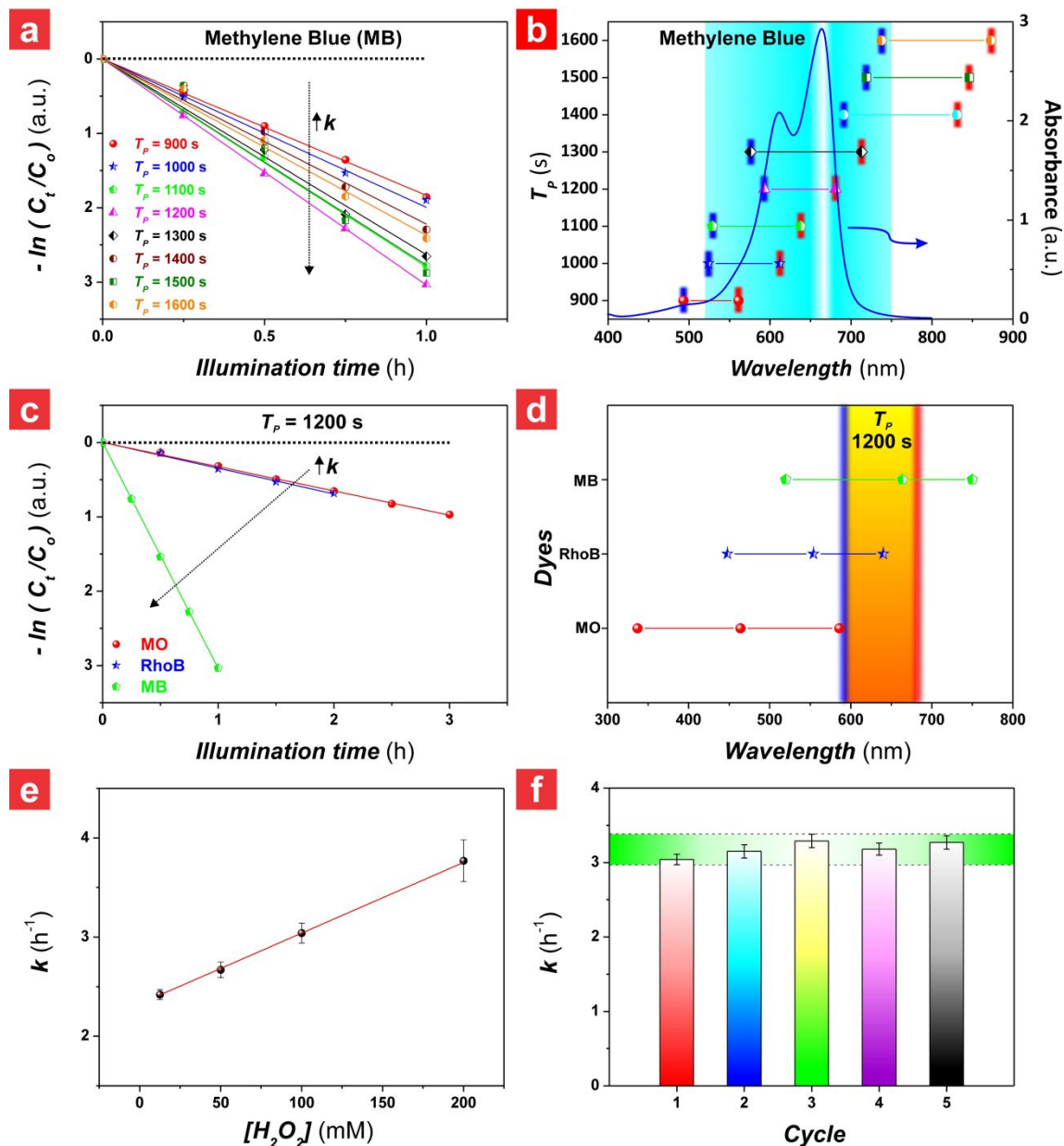


Figure 4. Photocatalytic assessment of TiO₂-NAA-DBRs as a function of anodization period (T_p), type of organic molecule, concentration of hydrogen peroxide (H₂O₂) solution, and recyclability (note: error bars in (a), (c), (e), and (f) correspond to standard deviation from $n = 3$ independent experiments). a) Photocatalytic degradation kinetics of methylene blue (MB) by TiO₂-NAA-DBRs produced with T_p from 900 to 1600 s with $\Delta T_p = 100$ s under controlled irradiation conditions (note: black dotted line denotes the photodegradation of the corresponding organic in a control NAA-DBR fabricated without photoactive TiO₂ layers). b) Relative position of the blue and red edges of the characteristic photonic stopband (PSB) of TiO₂-NAA-DBRs from (a) with respect to the absorbance band of MB (note: white gap inside the absorbance band of MB denotes the band maximum of MB – $\lambda_{abs-MB} = 664$ nm while blue and red vertical lines on the PSB correspond to the position of the blue and red edges of the PSB, respectively). c) Photocatalytic degradation kinetics of methyl orange (MO), rhodamine B (RhoB), and methylene blue (MB) by TiO₂-NAA-DBRs produced with $T_p = 1200$ s under controlled irradiation conditions (note: black dotted line denotes the photodegradation of the corresponding organic in a control NAA-DBR

fabricated without photoactive TiO₂ layers). d) Relative position of absorbance bands of model organics from (c) with the characteristic PSB of TiO₂-NAA-DBRs produced with $T_p = 1200$ s (note: the blue and red vertical lines on the PSB correspond to the position of the blue and red edges of the PSB, respectively). e) Linear correlation between the kinetic constant (k) and the concentration of H₂O₂ ([H₂O₂]) used in this study. f) Reusability test of TiO₂-NAA-DBRs produced with $T_p = 1200$ s on the photodegradation of MB under simulated solar light irradiation (note: horizontal bar corresponds to the standard deviation between the lowest and highest value of k).

Table 1. Effect of the relative position of the blue and red edges of the characteristic PSB and the total anodization time of TiO₂-NAA-DBRs fabricated with various T_p on the kinetic constant (k) for the photodegradation of MB molecules (note: error values correspond to standard deviation from $n = 3$ independent experiments).

Anodization Period (s)	900	1000	1100	1200	1300	1400	1500	1600
k (h ⁻¹)	1.83 ± 0.01	2.00 ± 0.06	2.80 ± 0.04	3.04 ± 0.01	2.63 ± 0.10	2.22 ± 0.09	2.77 ± 0.15	2.37 ± 0.08
Edge Nearest to the Peak	Red	Red	Red	Red	Red	Blue	Blue	Blue
Distance of Nearest Edge to the Peak (nm)	103	52	26	17	49	27	55	74
Total Anodization Time (h)	38.5	42.7	46.8	51.0	55.2	59.3	63.5	67.7

To summarize, the photocatalytic performance of TiO₂-NAA-DBRs is enhanced by the “slow photon” effect when the edges of the PSB fall within the absorbance range of MB. This enhancement is more significant when the red edge of the PSB of TiO₂-NAA-DBRs is at its closest to the absorbance band maximum of MB. Nevertheless, the thickness of the PC platform does play a more significant role in enhancing the photocatalytic properties of TiO₂-NAA-DBRs when the PSB is misaligned with the absorbance band of the model organic molecule. An optimum combination of relative position between the red edge of the PC’s PSB and the thickness of the PC platform boosts photocatalytic reactions, making an efficient and rational utilization of the “slow photon” effect and the physical properties of these photocatalysts.

3.5. Effect of Type of Organic Molecule on the Photocatalytic Performance of TiO₂-NAA-DBRs. The effect of the type and characteristics of organic molecules on the photocatalytic

1
2
3 performance of TiO₂-NAA-DBRs was investigated by assessing the photocatalytic degradation
4 of three model organics with well-defined absorbance bands across the visible spectral range
5 (i.e. MO, RhoB, and MB). TiO₂-NAA-DBRs produced with $T_p = 1200$ s were used as
6 photocatalyst platforms to study and identify “slow photon” effects associated with the relative
7 position between the edges of the PCs’ PSB and the absorbance and characteristics of the model
8 organic molecules. **Figures 4c and d** and **Table 2** summarize the effect of the spectral
9 arrangement between the absorbance bands of these model organic molecules and the position
10 of the edges of the PSB of TiO₂-NAA-DBRs, using their respective photodegradation rate as
11 an indicator of enhancements by “slow photon” effect. The k values for the photodegradation
12 of MO, RhoB, and MB by TiO₂-NAA-DBRs produced with $T_p = 1200$ s were 0.32 ± 0.01 , 0.35
13 ± 0.01 , and 3.04 ± 0.01 h⁻¹, respectively (**Figure 4c**). The highest k value was achieved by the
14 photodegradation of MB, which was degraded at a ~88 and 89% faster rate than RhoB and
15 MO, respectively. As **Figure 4d** and **Table 2** indicate, the characteristic PSB of TiO₂-NAA-
16 DBRs fabricated with $T_p = 1200$ s falls completely inside the absorbance range of MB.
17 However, only the blue part of the PSB partially overlaps with the absorbance band of RhoB,
18 and it is practically misaligned with the MO’s absorbance range. The red edge of the PSB of
19 these TiO₂-NAA-DBRs is located near the absorbance band of MB (i.e. ~17 nm away), while
20 its blue edge is located within the range of the absorbance band of RhoB (i.e. ~39 nm away)
21 and well-removed from the absorbance band of MO (i.e. ~129 nm away). As demonstrated in
22 the previous section, the red edge of the PSB plays is more significant than the blue edge in
23 enhancing photocatalytic reactions by “slow photon” effect. Our results confirm this hypothesis
24 as indicated by the analysis of the relative positions of the red edge of the PC’s PSB and the
25 absorbance band of these model molecules.

26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56 It is worth noting that the charge of the organic molecule and its interaction with the surface
57 charge of TiO₂-NAA-DBRs are also important contributing factors that impact on the overall
58
59
60

1
2
3 photodegradation rates achieved by these photocatalyst platforms. **Table S1 (Supporting**
4
5 **Information)** collates the charge of the model organic molecules used in this study, where
6
7 MO, RhoB, and MB are negatively, positively, and positively charged, respectively. The
8
9 surface of the photoactive TiO₂ layer deposited onto the inner surface of NAA-DBRs is
10
11 negatively charged at pH 5.5, the pH of the aqueous solution at which these photo-chemical
12
13 reactions were performed. The negatively charged surface of TiO₂ would have high affinity for
14
15 positively charged RhoB and MB molecules.^{1,4} This would increase the total number of
16
17 molecules adsorbed onto the surface of TiO₂, boosting the overall photocatalytic degradation
18
19 rate of the system. Conversely, interaction between the negatively charged surface of the
20
21 photoactive TiO₂ layers and negatively charged MO molecules is poor due to electrostatic
22
23 repulsion. The reduced amount of MO molecules present within the vicinity of the photoactive
24
25 layer would lead to a significant reduction of the system's performance. Another factor to
26
27 consider is the intensity of the absorption bands of MO, RhoB, and MB. As **Figure S3**
28
29 indicates, the absolute absorption intensity of MO, RhoB and MB at their central position
30
31 maxima ($\lambda_{\text{abs-MO}} = 464$ nm, $\lambda_{\text{abs-RhoB}} = 554$ nm, and $\lambda_{\text{abs-MB}} = 664$ nm) are ~2.8, 3.6 and 1.5 a.u.,
32
33 respectively. RhoB (~3.6 a.u.) and MO (~2.8 a.u.) molecules absorb incoming light more
34
35 efficiently than that MO (~1.5 a.u.). At these spectral regions, RhoB and MO molecules absorb
36
37 most of the incoming light that propagates through the aqueous organic solutions before it
38
39 reaches the surface of the TiO₂-NAA-DBRs. This screening effect reduces the overall
40
41 photocatalytic performance of the material due to an inefficient use of photons in the
42
43 semiconductor band. Therefore, overall photocatalytic degradation rates provided by TiO₂-
44
45 NAA-DBRs are also dependent on the nature of the organic molecule, the electrostatic
46
47 interactions surface-molecule and the relative positioning between the edges of the PSB and
48
49 the absorbance band of the organics. These observations are in good agreement with our
50
51
52
53
54
55
56
57
58
59
60

previous study using NAA gradient-index filters as model photonic crystal platforms⁴, which is a further evidence to support our conclusions.

Table 2. Values of the kinetic constant (k) for the photodegradation of three organics (i.e. MO, RhoB, and MB) by TiO₂-NAA-DBR with $T_p = 1200$ s (note: error values correspond to standard deviation from $n = 3$ independent experiments).

Organic Molecule	MO	RhoB	MB
k (h ⁻¹)	0.32 ± 0.01	0.35 ± 0.01	3.04 ± 0.01

3.6. Effect of Additive Concentration and Assessment of Reusability on the Photocatalytic

Performance of TiO₂-NAA-DBRs. The relationship between the concentration of H₂O₂ ([H₂O₂]) and the photocatalytic degradation performance of TiO₂-NAA-DBRs was studied by assessing the photocatalytic degradation of MB by TiO₂-NAA-DBRs produced with $T_p = 1200$ s. In this experiment, the concentration of H₂O₂ was varied from 12.5, 50, 100 to 200 mM (**Figure 4e**). The kinetic constants for this photocatalytic reaction as a function of [H₂O₂] were determined to be 2.42 ± 0.05 , 2.67 ± 0.08 , 3.04 ± 0.10 , and 3.77 ± 0.21 h⁻¹, respectively. A linear fitting between the k values and [H₂O₂] indicates that the former parameter increases with the latter at a rate of 0.01 ± 0.00 mM h⁻¹. This correlation can be associated with the higher number of ·OH radicals photogenerated in the inner surface of TiO₂-NAA-DBRs with increasing [H₂O₂], which speed up the degradation of MB molecules. Reusability is another aspect of paramount importance to minimize the technological translation costs associated with the bench-to-field translation of photocatalyst materials. Reusability of TiO₂-NAA-DBRs was tested using the same TiO₂-NAA-DBR platform (i.e. $T_p = 1200$ s) in all five consecutive cycles of photodegradation, in which fresh MB solutions were photodegraded under simulated solar light irradiation for 1 h per cycle. The results summarized in **Figure 4f** show that k fluctuates from 3.04 ± 0.07 to 3.29 ± 0.09 h⁻¹ between the first and fifth photodegradation cycle, demonstrating that TiO₂-NAA-DBRs provide a relatively similar performance after several

1
2
3 cycles of use. The average k value for the five photodegradation cycles is $3.18 \pm 0.29 \text{ h}^{-1}$, where
4
5 the photocatalytic conversion ratio of TiO_2 -NAA-DBRs in the photodegradation of MB is
6
7 $\sim 96\%$ under simulated solar light irradiation (**Table S2 – Supporting Information**). These
8
9 results demonstrate that TiO_2 -NAA-DBRs possess high photocatalytic activity, stability and
10
11 reusability, which are required properties for real-life photocatalysis applications.
12
13
14

15 **3.7. Assessment of Photocatalytic Degradation of 4-Chlorophenol by TiO_2 -NAA-DBRs.**

16
17 Organic dyes are widely used model organics to assess the photocatalytic degradation
18
19 performance of photocatalyst PC structures under visible light irradiation.^{1,4-5,37} However,
20
21 resilient organic pollutants such as pesticides have absorbance bands in the UV spectral region.
22
23 This factor limits substantially the photocatalytic performance of PC structures with PSB in
24
25 the visible range to degrade these chemicals under visible-NIR light irradiation. The ability of
26
27 TiO_2 -NAA-DBRs to degrade real-life resilient organic pollutants was assessed by studying the
28
29 photodegradation of 4-chlorophenol (4-CP) under controlled visible-NIR irradiations
30
31 conditions. 4-CP is used as intermediate in the production of pharmaceuticals, agricultural
32
33 products, biocides, and paints and it is classified as a dangerous substance that can lead to
34
35 irreversible changes in the aquatic ecosystems. 4-CP has a distinctive and well-resolved
36
37 absorbance band located at 225 nm (**Figure S4 – Supporting Information**) to provide a direct
38
39 relationship between its absorbance at 225 nm and the concentration of 4-CP in the solution as
40
41 determined by the calibration line shown in **Figure S7 (Supporting Information)**. The effect
42
43 of relative position of the blue and red edges of the PSB with the absorbance band of 4-CP on
44
45 the photodegradation of 4-CP by TiO_2 -NAA-DBRs was first studied using a set of TiO_2 -NAA-
46
47 DBRs fabricated with $T_p = 900, 1200, \text{ and } 1600 \text{ s}$ as model PC platforms. **Figure 5a** shows
48
49 dynamic photodegradation of 4-CP by these semiconductor PCs, while **Table 3** summarizes
50
51 the kinetic constants estimated for TiO_2 -NAA-DBRs produced with $T_p = 900, 1200, \text{ and } 1600$
52
53 s calculated from linear fittings, which were $0.15 \pm 0.01, 0.14 \pm 0.01, \text{ and } 0.03 \pm 0.00 \text{ h}^{-1}$,
54
55
56
57
58
59
60

1
2
3 respectively. These results indicate that TiO₂-NAA-DBRs produced with $T_P = 900$ and 1200 s
4
5 provide the best photocatalytic performances, where the former model PCs showed a ~7%
6
7 higher performance than that achieved by their equivalents produced with longer anodization
8
9 period. In contrast, TiO₂-NAA-DBRs produced with $T_P = 1600$ s showed the worst
10
11 photocatalytic performance, which was ~79 to ~80% worse than that of their 1200 and 900 s
12
13 counterparts, respectively. **Figure 5b** shows the relative position of the edges of characteristic
14
15 PSB of these semiconductor PCs with the absorbance band of 4-CP as a function of T_P . The
16
17 PSB of all these TiO₂-NAA-DBRs falls completely outside of the absorbance range of 4-CP
18
19 (**Figure S3**). Under such a configuration, the photocatalytic degradation of 4-CP by TiO₂-
20
21 NAA-DBRs should not depend on the “slow photon” effect but rely solely upon the total
22
23 thicknesses of TiO₂-NAA-DBR platforms. Therefore, the thicker the TiO₂-NAA-DBR
24
25 platform the better the photocatalytic performance. However, the obtained k values indicate
26
27 that the closer the PSB of TiO₂-NAA-DBRs is to the UV absorbance band of the model
28
29 pesticide the faster the degradation rate achieved by this photocatalyst system (i.e. higher k
30
31 value).

32
33 **Table 3.** Values of the kinetic constant (k) for the photodegradation of 4-CP by TiO₂-NAA-DBRs
34
35 produced with $T_P = 900$, 1200, and 1600 s (note: error values correspond to standard deviation from n
36
37 = 3 independent experiments).

Anodization Period (s)	900	1200	1600
k (h ⁻¹)	0.15 ± 0.01	0.14 ± 0.01	0.03 ± 0.00

38
39 This result is demonstrated to be independent on the thickness of the TiO₂-NAA-DBR platform
40
41 (i.e. $T_P = 900$ s – $t_{An} = 38.5$ h; $T_P = 1200$ s – $t_{An} = 51.0$ h; $T_P = 1600$ s – $t_{An} = 67.7$ h). We
42
43 hypothesize that this effect can be attributable to “slow photon” effect-driven enhancement of
44
45 the photocatalysis performance achieved by these TiO₂-NAA-DBRs. **Figure 5b** further
46
47 supports this hypothesis since the PSB of TiO₂-NAA-DBRs produced with $T_P = 900$ and 1200
48
49 s falls completely under the visible spectral region, while the PSB of TiO₂-NAA-DBRs
50
51 fabricated with $T_P = 1600$ s is almost entirely located within the NIR region of the spectrum.
52
53
54
55
56
57
58
59
60

1
2
3 **Figure S5** shows that ~65% of the artificial illumination used in our study corresponds to
4 visible light, while the remaining ~35% of illumination is NIR light. Therefore, it is inferred
5 that TiO₂-NAA-DBRs with PSB within the visible spectral region can collect and utilize more
6 efficiently photons from the high irradiance visible region to generate carriers for
7 photocatalytic degradation of 4-CP. This also contributes to the superior performance achieved
8 by TiO₂-NAA-DBRs produced with shorter T_p , since the PSB of these PCs is located in the
9 visible spectral range. Note that the overall photocatalytic degradation of 4-CP molecules is
10 low as compared to that achieved for MO, RhoB, and MB. However, 4-CP is a chemically
11 resilient and negatively charged molecule (**Table S1**) that is electrostatically repulsed by the
12 negatively charged inner surface of TiO₂-NAA-DBRs. This minimizes the number of 4-CP
13 molecules that are absorbed onto the photocatalyst platform surface, reducing the overall
14 photodegradation performance of the system. Kim and Choi⁵⁸ studied the visible-light-induced
15 degradation reaction of 4-CP in aqueous suspension, using pure TiO₂ powder as photocatalyst
16 platform material. Their observations indicate that the surface complexation between phenolic
17 compounds and TiO₂ appears to be responsible for the visible light reactivity. According to this
18 photodegradation mechanism, a direct electron transfer from surface-complexed phenol groups
19 to the conduction band of the TiO₂ coating upon absorbing visible light is the responsible factor
20 to initiate the oxidative degradation of 4-CP.
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43

44 The performances of photocatalyst materials are typically assessed using ultrapure water-based
45 aqueous solutions. However, the effect of the composition and complexity of the aqueous
46 matrix on the performance of photocatalysts is a critical aspect to consider for real-life
47 applications and for the translation of fundamental advances in photocatalysis into practical
48 systems that can address real-world problems. Therefore, the effect of the media composition
49 on the photocatalytic performance of a set of TiO₂-NAA-DBRs produced with $T_p = 1200$ s was
50
51
52
53
54
55
56
57
58
59
60

assessed studying the degradation of 4-CP in various matrices (i.e. Milli-Q H₂O, tap H₂O, Torrens river H₂O, and 10 g L⁻¹ NaCl aqueous solution).

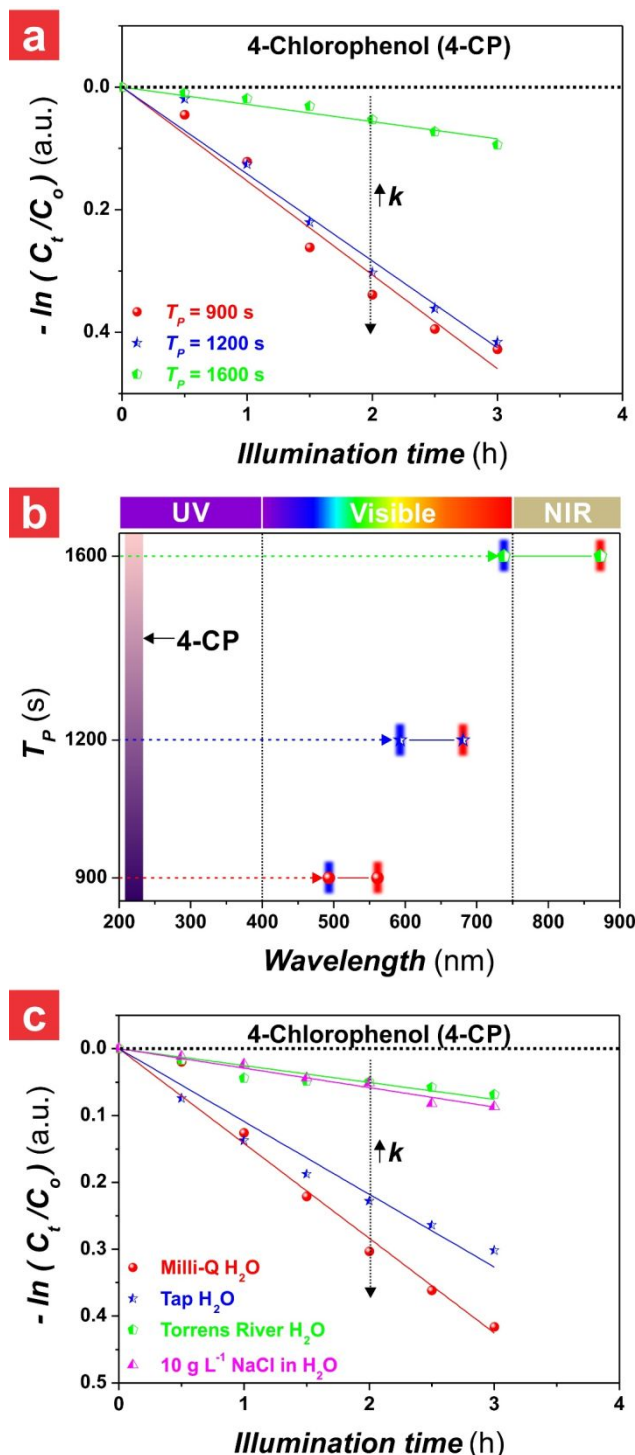


Figure 5. Photocatalytic assessment of TiO₂-NAA-DBRs on the photodegradation of 4-chlorophenol (4-CP) as a function of anodization period (T_p) and aqueous matrix composition (note: error bars in (a) and (c) correspond to standard deviation from $n = 3$ independent experiments). a) Photocatalytic degradation kinetics of 4-CP by TiO₂-NAA-DBRs produced with $T_p = 900, 1200,$ and 1600 s under controlled irradiation conditions (note: black dotted

line denotes the photodegradation of the 4-CP in a control NAA-DBR fabricated without photoactive TiO₂ layers). b) Relative position of the blue and red edges of the characteristic photonic stopband (PSB) of TiO₂-NAA-DBRs from (a) with the absorbance band of 4-CP (note: the blue and red vertical lines on the PSB correspond to the position of the blue and red edges of the PSB, respectively). c) Photocatalytic degradation kinetics of 4-CP in different aqueous matrices by TiO₂-NAA-DBRs produced with $T_p = 1200$ s under controlled irradiation conditions (note: black dotted line denotes the photodegradation of 4-CP in a control NAA-DBR fabricated without photoactive TiO₂ layers).

Figure 5c shows dynamic photodegradation of 4-CP in these matrices and **Table 4** summarizes the obtained k values, which were estimated to be 0.14 ± 0.01 , 0.11 ± 0.01 , 0.025 ± 0.001 , and 0.029 ± 0.002 h⁻¹, respectively. These results indicate that this photo-chemical reaction achieves its best performance when the aqueous matrix is Milli-Q H₂O ($k = 0.14 \pm 0.01$ h⁻¹). This result is expected since this matrix does not have interfering molecules that can potentially hinder the interaction between 4-CP molecules and the inner functional surface of TiO₂-NAA-DBRs. The k value for the photodegradation of 4-CP in tap H₂O is the second highest and it was found to perform ~21% less efficiently than in Milli-Q H₂O under simulated solar light irradiation ($k = 0.11 \pm 0.01$ h⁻¹). When the photocatalytic degradation of 4-CP is performed in environmental water from the Torrens river (Adelaide, Australia) and a Milli-Q H₂O-based 10 g L⁻¹ NaCl solution, the k values were found to be ~73 and 81% lower than those obtained in less complex matrices (i.e. $k = 0.025 \pm 0.001$ and 0.029 ± 0.002 h⁻¹, respectively). This result indicates that this photo-chemical reaction is hindered when it is conducted in complex matrices. This significant difference in photocatalytic degradation of 4-CP by TiO₂-NAA-DBRs can be attributable to interfering ions and molecules present in these complex solutions.

Table 4. Values of the kinetic constant (k) for the photodegradation of 4-CP in four different matrices (i.e. Milli-Q H₂O, tap H₂O, Torrens river H₂O, and 10 g L⁻¹ NaCl aqueous solution) by TiO₂-NAA-DBRs produced with $T_p = 1200$ s (note: error values correspond to standard deviation from $n = 3$ independent experiments).

Matrix	Milli-Q H ₂ O	Tap H ₂ O	Torrens river H ₂ O	10 g L ⁻¹ NaCl
k (h ⁻¹)	0.14 ± 0.01	0.11 ± 0.00	0.025 ± 0.001	0.029 ± 0.002

Milli-Q H₂O and tap H₂O matrices are relatively free from ions and molecules, although the latter contains some small concentration of ions such as Ca²⁺, Na⁺, K⁺, Mg²⁺, Fe²⁺, and Cl⁻ that

1
2
3 slightly interfere with the photodegradation of 4-CP, as indicated by the k values. When this
4 light-driven reaction is performed in a saline aqueous solution (i.e. $10 \text{ g L}^{-1} \text{ NaCl}$), salt
5 molecules dissociate in water to form Na^+ and Cl^- ions. A high concentration of these ions
6 inside the nanopores of TiO_2 -NAA-DBRs is demonstrated to slow down this reaction by
7 hindering interactions between the inner surface of TiO_2 -NAA-DBRs and water molecules to
8 form $\cdot\text{OH}$ radicals that subsequently oxidize absorbed 4-CP molecules into bi-products.
9 Furthermore, presence of these ions also reduces the total amount of 4-CP molecules absorbed
10 onto the negatively charged inner surface of TiO_2 -NAA-DBRs, decreasing significantly the
11 overall performance of the system. As the k values indicate, the photocatalytic degradation of
12 4-CP in Torrens river H_2O is slightly worse than that obtained in the $10 \text{ g L}^{-1} \text{ NaCl}$ aqueous
13 solution, due to the presence of ions and organic molecules that interfere the formation of $\cdot\text{OH}$
14 radicals and compete with the absorption of 4-CP molecules onto the inner surface of TiO_2 -
15 NAA-DBRs. This analysis reveals that the photocatalytic performance of TiO_2 -NAA-DBRs in
16 degrading 4-CP molecules is thus highly affected by the presence of interfering ions and
17 organic molecules. However, TiO_2 -NAA-DBRs are still efficient enough to degrade a highly
18 resilient environmental pollutant in complex aqueous matrices. This is a clear demonstration
19 of the potential of these semiconductor PC structures for real-life applications.
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42

43 **3.8. Photocatalytic Degradation Mechanism.** The experimental results obtained in this study
44 allow us to propose a photocatalytic degradation mechanism that explains the performance of
45 TiO_2 -NAA-DBRs. These NAA-based PC structures collect photons from high irradiance
46 spectral region (i.e. visible and NIR), which are efficiently utilized by the photoactive TiO_2
47 layers to speed up photocatalytic reaction rates, as indicated by the degradation of model
48 organic molecules. In this process, charge carriers (e^-/h^+) are generated and separated upon
49 light irradiation to the conduction band and valence band of TiO_2 , respectively. These charge
50 carriers are subsequently transferred to the surroundings of the nanopores' surface and react
51
52
53
54
55
56
57
58
59
60

1
2
3 with redox species to produce reactive oxidation species (i.e. $\cdot\text{OH}$ radicals), which decompose
4 organic molecules absorbed onto or close to the inner surface of the nanopores.⁵⁹ When H_2O_2
5 molecules are added to the matrix solution, electrons at the conduction band react with H_2O_2
6 to form $\cdot\text{OH}$ radicals and ^-OH ions, which can be further oxidized to $\cdot\text{OH}$ radicals by the
7 photogenerated holes at the valence band of TiO_2 . Photogenerated holes also oxidize H_2O
8 molecules to form $\cdot\text{OH}$ radicals, which decompose organic molecules into CO_2 and H_2O , which
9 are harmless to the environment. Our results demonstrate that the photocatalytic decomposition
10 rate at the TiO_2 layers can be significantly enhanced by rationally engineering the underlying
11 NAA-DBR structure to increase photon-to-electron conversion rates at the TiO_2 functional
12 layers. Photons absorbed by the structure of NAA-DBRs propagate with reduced group
13 velocity and localize near the PSB's edges, resulting in longer lifespan of photons at these
14 spectral regions. These photons can be subsequently utilized by the photoactive TiO_2 layers to
15 generate extra carriers and accelerate light-driven redox reactions occurring within the
16 nanopores of TiO_2 -NAA-DBRs. The "slow photon" effect is strongly dependent on the relative
17 position of the PSB's edges with respect to the absorbance band of model organic molecules.
18 For instance, the photocatalytic enhancement was found to be maximum when the PSB's red
19 edge falls completely within the absorbance band maximum of the organic molecules. Our
20 results also indicate that positioning the blue edge of the PSB towards the absorbance band
21 maximum of these organic molecules can enhance photocatalytic reactions by "slow photon"
22 effect too, although in a less efficient manner than that achieved by the red edge due to the
23 higher localization of slow photons at the high refractive index section of the PC structure (i.e.
24 semiconductor – red edge).

25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60
The "slow photon" enhancement is dramatically reduced when the distance between the PSB's
edges and the absorbance band of organic molecules is increased. Under this arrangement (i.e.
partial overlapping between the PC's PSB and the absorbance band of the organic molecule),

1
2
3 the contribution of the “slow photon” effect to the overall photocatalytic enhancement is weak,
4
5 and other factors such as the total pore length of the composite PC structure are found to have
6
7 a more significant contribution towards the photocatalytic performance of the PC structure.
8
9 However, the assessment on the photodegradation of 4-CP molecules (i.e. absorbance band in
10
11 the UV range) indicates that, when the configuration of the system is such that the PSB falls
12
13 completely outside the absorbance band of the organic molecule, the closer the PSB is from
14
15 the absorbance band the more efficient the photocatalytic PC system is, independently of its
16
17 overall thickness. However, other factors such as percentage of high irradiance spectral regions
18
19 also contribute significantly to the overall performance of these semiconductor PCs. Our study
20
21 also establishes that the nature of the organic molecule is another important contributing factor
22
23 to the efficiency of these light-driven reactions.
24
25
26
27
28

29 **3.9. Comparative Analysis with Benchmark Photocatalyst Platforms.** Table 5 compiles a
30
31 summary of representative studies using benchmark photocatalyst materials with and without
32
33 PC structure, the performance of which was assessed under visible light irradiation conditions.
34
35 Multiple studies reported on the photocatalytic performance of P25 TiO₂ nanoparticles to
36
37 photodegrade MO, RhoB, MB, and 4-CP under visible light irradiation conditions.^{1,60} P25 TiO₂
38
39 is a benchmark photocatalyst material that features anatase crystallographic phase and only
40
41 absorbs light in the UV spectral region. The photocatalytic degradation rates reported for P25
42
43 TiO₂ nanoparticles when photodegrading these model organics were $k_{\text{MO}} = 0.00 \text{ h}^{-1}$, $k_{\text{RhoB}} =$
44
45 0.17 h^{-1} , $k_{\text{MB}} = 0.64 \text{ h}^{-1}$, and $k_{\text{4-CP}} = 0.0037 \text{ h}^{-1}$. These values indicate that TiO₂-NAA-DBRs
46
47 substantially outperform P25 TiO₂ nanoparticles in the degradation of these organic molecules
48
49 under visible light irradiation, with a photocatalytic enhancement of 100, 51, 79, and 75%,
50
51 respectively. Though a direct comparison could not be entirely correct due to differences in
52
53 experimental conditions (e.g. irradiation spectral distribution, power density, catalyst loading,
54
55
56
57
58
59
60

etc.), this comparison indicates the potential of TiO₂-NAA-DBRs as efficient photocatalyst platforms.

Table 5. Compilation of representative kinetic constant (k) values for the photodegradation of MO, RhoB, MB, and 4-CP molecules by various photocatalysts.

Photocatalyst	k (h ⁻¹)				Ref.
	MO	RhoB	MB	4-CP	
P25 TiO ₂ Nanoparticles	0.00	0.17	0.64	0.037	1, 60
TiO ₂ Inverse Opal	0.01	0.47	1.32	-	1
ZnO Inverse Opal	0.01	0.13	1.49	0.00	30
TiO ₂ -NAA-GIFs	0.25	0.39	2.10	-	4
TiO ₂ -NAA-DBRs	0.32	0.35	3.04	0.15	This Study

TiO₂ inverse opals feature a 3D PC structure and have been devised as promising photocatalyst platforms due to their well-defined and relatively controllable characteristic PSB. The PC structure of semiconductor inverse opals enables the utilization of the “slow photon” effect to enhance photocatalytic reactions. Zheng *et al.*¹ fabricated a set of TiO₂-based inverted opal structures featuring various pore sizes (i.e. from 270 to 550 nm) and assessed the photodegradation of three model organic dyes (i.e. RhoB, MO, and MB) under visible light irradiation. The photocatalytic performance achieved by this system was $k_{\text{MO}} = 0.01 \text{ h}^{-1}$, $k_{\text{RhoB}} = 0.47 \text{ h}^{-1}$, and $k_{\text{MB}} = 1.32 \text{ h}^{-1}$, respectively. Although these TiO₂ inverse opal structures outperform TiO₂-NAA-DBRs by ~34% in the photodegradation of RhoB, TiO₂-NAA-DBRs show enhanced photocatalytic performances in the photodegradation of MO and MB (i.e. ~97 and ~57% superior performance, respectively). Other types of inverse opal PC structures have been explored for enhanced photon-to-electron conversion rates through the “slow photon” effect. For instance, ZnO-based inverse opals with PSB positioned in the visible range (i.e. 510,

1
2
3 600, and 720 nm) were fabricated by systematically modifying the pore size of the
4 semiconductor structure from 260 to 320 nm. The photocatalytic performance of these PCs was
5 assessed by the degradation of MO, RhoB, MB, and 4-CP under visible light irradiation.³⁰
6
7 These ZnO inverse opal structures achieved photocatalytic degradation rates of $k_{\text{MO}} = 0.01 \text{ h}^{-1}$,
8 $k_{\text{RhoB}} = 0.13 \text{ h}^{-1}$, $k_{\text{MB}} = 1.49 \text{ h}^{-1}$, and $k_{\text{4-CP}} = 0.00 \text{ h}^{-1}$ for MO, RhoB, MB, and 4-CP molecules,
9
10 respectively. A comparison with our results (**Table 5**) indicates that TiO₂-NAA-DBR
11 structures provide superior properties than ZnO inverse opals to photodegrade these organic
12 molecules, with an enhancement of 97, 63, 51, and 100%, respectively.
13
14

15
16
17 Our group developed NAA-based gradient-index filters (NAA-GIFs) PC structures with
18 deposited photoactive layers of TiO₂.⁴ TiO₂-NAA-GIFs were produced with varying
19 anodization period (i.e. from 650 to 850 s) and used as photocatalyst platforms to degrade MO,
20 RhoB, and MB under visible-NIR irradiation. The photocatalytic decomposition rates achieved
21 for MO, RhoB, and MB were $k_{\text{MO}} = 0.25 \text{ h}^{-1}$, $k_{\text{RhoB}} = 0.39 \text{ h}^{-1}$, and $k_{\text{MB}} = 2.10 \text{ h}^{-1}$, respectively.
22
23 Although the photocatalytic performance of TiO₂-NAA-GIFs for RhoB was 11% better than
24 that achieved by TiO₂-NAA-DBRs, TiO₂-NAA-DBRs show more efficient performance for
25 MO and MB, with an enhancement of 22 and 31%, respectively. In general, TiO₂-NAA-DBRs
26 perform more efficiently than TiO₂-NAA-GIFs under visible-NIR irradiation. This
27 enhancement may be attributable to the more efficient light collection associated with the
28 broader and intense characteristic PSB of NAA-DBR structures.
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45

46
47 To summarize, this comparison demonstrates that the photocatalytic performance of TiO₂-
48 NAA-DBRs is generally superior to that of existing photocatalyst systems. The optical and
49 optoelectronic properties of these semiconductor composite PC structures can be precisely
50 tuned across the spectral regions to achieve enhanced performances in photocatalysis by
51 rationally managing photons at the nanoscale.
52
53
54
55
56
57
58

59 CONCLUSIONS

1
2
3 This study provides new insights into the capability of NAA-based composite
4 semiconductor photonic crystal structures to enhance and accelerate photocatalytic reactions
5 by the “slow photon” effect. NAA-DBRs with varying anodization period were fabricated by
6 stepwise pulse anodization and subsequently functionalized with photoactive TiO₂ layers. The
7 optical properties of these model nanoporous semiconductor PCs can be precisely tuned across
8 the spectral regions to identify light–matter interactions that lead to unprecedented
9 enhancements in photocatalytic reactions. “Slow photon” effects in TiO₂-NAA-DBRs were
10 investigated by model photo-chemical reactions, using the photodegradation of methyl orange,
11 rhodamine B, methylene blue, and 4-chlorophenol under controlled visible-NIR light
12 irradiation. Our study demonstrates that TiO₂-NAA-DBRs degrade these organic molecules
13 efficiently with high photocatalytic performances (i.e. $k_{\text{MO}} = 0.32 \pm 0.01 \text{ h}^{-1}$, $k_{\text{RhOB}} = 0.35 \pm$
14 0.01 h^{-1} , $k_{\text{MB}} = 3.04 \pm 0.01 \text{ h}^{-1}$ and $k_{\text{4-CP}} = 0.15 \pm 0.01 \text{ h}^{-1}$). TiO₂-NAA-DBRs demonstrate
15 outstanding photocatalytic performances as compared to other benchmark photocatalyst
16 platforms such as P25 TiO₂ nanoparticles and TiO₂ and ZnO inverted opal PCs.
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34

35 Enhancement of photodegradation rates in TiO₂-NAA-DBRs is found to be optimal
36 when the red edge of the PSB is in close proximity to or falls entirely within the absorbance
37 band of the model organic molecules. However, the photocatalytic enhancement by the “slow
38 photon” effect becomes weaker with increasing distance between the edges of the PSB and the
39 absorbance band of the organic molecules. When the PSB partially overlaps with the
40 absorbance band of the organic compound, a compromise between the total pore length of the
41 PC structure and the “slow photon” effect in the photocatalytic enhancement can provide
42 photocatalytic enhancements by an optimal combination of these factors. Our study also
43 indicates that, in the case of organics with absorbance bands in the UV spectral region, when
44 the PC’s PSB is in the visible or NIR regions, the photocatalytic performance of TiO₂-NAA-
45 DBRs is only associated with the relative distance between the absorbance band and the PC’s
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

1
2
3 PSB and the percentage of visible-NIR irradiation, and independent on the total pore length of
4 the PC structure. Furthermore, our study demonstrates that interferences from ions and
5 molecules present in the aqueous matrix strongly decrease the overall photocatalytic
6 degradation rate of TiO₂-NAA-DBRs. However, these PC structures are still able to
7 photodegrade resilient pesticide molecules such as 4-chlorophenol in complex aqueous
8 matrices. The charge of the organic molecules and the concentration of hydrogen peroxide
9 solution are also contributing factors in dictating the overall photocatalytic performance of
10 TiO₂-NAA-DBRs, where positively charged molecules (i.e. rhodamine B and methylene blue)
11 and higher concentration of hydrogen peroxide result in enhanced photocatalytic performances.
12 TiO₂-NAA-DBRs also provide high photostability and reusability in the photocatalytic
13 degradation of organic molecules and can maintain their outstanding performance after five
14 cycles.
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29

30
31 In summary, this study provides new opportunities to develop sustainable and high-
32 performing photocatalyst platforms based on surface-functionalized nanoporous anodic
33 alumina photonic crystals fabricated with a rational design of optical properties to attain an
34 efficient management of photons for photocatalysis.
35
36
37
38
39
40

41 AUTHORS INFORMATION

42 **Corresponding Authors**

43 **Professor Lluís F. Marsal**

44 Department of Electronic, Electric, and Automatics Engineering – Universitat Rovira i
45
46

47 Virgili
48
49

50 Phone: + 34 977559625
51

52 Email: lluis.marsal@urv.cat
53

54 Web page: <http://www.urv.cat/html/docencia-per-centre/general-94602760.php>
55

56 **Professor Nicolas H. Voelcker**

57 Monash Institute of Pharmaceutical Sciences – Monash University
58
59
60

1
2
3 Phone: + 61 03 9902 9097

4
5 Email: nicolas.voelcker@monash.edu

6
7 Web page: <https://research.monash.edu/en/persons/nicolas-voelcker>

8
9 **Professor Andrew Abell**

10 School of Chemistry and Physics – The University of Adelaide

11
12 Phone: + 61 8 8313 5652

13
14 Email: andrew.abell@adelaide.edu.au

15
16 Web page: <http://researchers.adelaide.edu.au/profile/andrew.abell#contact-details>

17
18
19 **Doctor Abel Santos**

20 School of Chemical Engineering – The University of Adelaide

21
22 Phone: +61 8 8313 1535

23
24 Email: abel.santos@adelaide.edu.au

25
26 Web page: <http://www.adelaide.edu.au/directory/abel.santos>

27
28
29 **Notes**

30
31
32 The authors declare no competing financial interest.

33
34 **ACKNOWLEDGMENT**

35
36
37 Authors thank the support provided by the Australian Research Council (ARC) through the
38 grant number CE140100003, the School of Chemical Engineering, the University of Adelaide
39 (DVCR ‘Research for Impact’ initiative), the Institute for Photonics and Advanced Sensing
40 (IPAS), the ARC Centre of Excellence for Nanoscale BioPhotonics (CNBP), the Spanish
41 Ministry of Economy and competitiveness TEC2015-71324-R (MINECO/FEDER), the
42 Catalan authority AGAUR 2017SGR1527, and ICREA under the ICREA Academia Award.
43 This work was performed in part at the Melbourne Centre for Nanofabrication (MCN) in the
44 Victorian Node of the Australian National Fabrication Facility (ANFF).
45
46
47
48
49
50

51
52 **ASSOCIATED CONTENT**

53
54 **Supporting Information.** Further information on the fabrication, surface functionalization and
55 photocatalytic performance of TiO₂-NAA-DBRs; the calibration lines correlating organic
56 molecules concentration and absorbance; transmission spectra of NAA-DBRs; absorbance
57
58
59
60

1
2
3 spectra of organic molecules; spectrum for the simulated solar light irradiation; digital pictures
4
5 of photodegraded MB solution; properties of organic molecules; results of reusability. This
6
7 material is available free of charge via the Internet at <http://pubs.acs.org>.
8
9
10
11
12
13
14
15
16
17
18
19
20

21 REFERENCES

- 22
23 1. Zheng, X.; Meng, S.; Chen, J.; Wang, J.; Xian, J.; Shao, Y.; Fu, X.; Li, D. Titanium Dioxide
24 Photonic Crystals with Enhanced Photocatalytic Activity: Matching Photonic Band Gaps of
25 TiO₂ to the Absorption Peaks of Dyes. *J. Phys. Chem. C* **2013**, *117*, 21263-21273.
26
27 2. Geng, Z.; Zhang, Y.; Yuan, X.; Huo, M.; Zhao, Y.; Lu, Y.; Qiu, Y. Incorporation of Cu₂O
28 nanocrystals into TiO₂ Photonic Crystal for Enhanced UV-Visible Light Driven Photocatalysis.
29 *J. Alloys Compd.* **2015**, *644*, 734-741.
30
31 3. Lu, Y.; Yu, H.; Chen, S.; Quan, X.; Zhao, H. Integrating Plasmonic Nanoparticles with TiO₂
32 Photonic Crystal for Enhancement of Visible-Light Driven Photocatalysis. *Environ. Sci.*
33 *Technol.* **2012**, *46*, 1724-1730.
34
35 4. Lim, S. Y.; Law, C. S.; Markovic, M.; Kirby, J. K.; Abell, A. D.; Santos, A. Engineering the
36 Slow Photon Effect in Photoactive Nanoporous Anodic Alumina Gradient-Index Filters for
37 Photocatalysis. *ACS Appl. Mater. Interfaces* **2018**, *10*, 24124-24136.
38
39 5. Toumazatou, A.; Arfanis, M. K.; Pantazopoulos, P.-A.; Kontos, A. G.; Falaras, P.; Stefanou,
40 N.; Likodimos, V. Slow-Photon Enhancement of Dye Sensitized TiO₂ Photocatalysis. *Mater.*
41 *Lett.* **2017**, *197*, 123-126.
42
43 6. Sheng, X.; Liu, J.; Coronel, N.; Agarwal, A. M.; Michel, J.; Kimerling, L. C. Integration of
44 Self-Assembled Porous Alumina and Distributed Bragg Reflector for Light Trapping in Si
45 Photovoltaic Devices. *IEEE Photonics Technol. Lett.* **2010**, *22*, 1394-1396.
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60

- 1
2
3 7. Guo, M.; Xie, K.; Wang, Y.; Zhou, L.; Huang, H. Aperiodic TiO₂ Nanotube Photonic
4 Crystal: Full-Visible-Spectrum Solar Light Harvesting in Photovoltaic Devices. *Sci. Rep.* **2014**,
5 *4*, 6442.
6
7
- 8
9 8. Guo, M.; Su, H.; Zhang, J.; Liu, L.; Fu, N.; Yong, Z.; Huang, H.; Xie, K. Broadband and
10 Omnidirectional Light Harvesting Enhancement in Photovoltaic Devices with Aperiodic TiO₂
11 Nanotube Photonic Crystal. *J. Power Sources* **2017**, *345*, 12-20.
12
13
- 14
15 9. Dronov, R.; Jane, A.; Shapter, J. G.; Hodges, A.; Voelcker, N. H. Nanoporous Alumina-
16 Based Interferometric Transducers Ennobled. *Nanoscale* **2011**, *3*, 3109-3114.
17
18
- 19 10. Wijnhoven, J. E. G. J.; Vos, W. L. Preparation of Photonic Crystals Made of Air Sphers in
20 Titania. *Science* **1998**, *281*, 802-804.
21
22
- 23 11. Yablonovitch, E. Inhibited Spontaneous Emission in Solid-State Physics and Electronics.
24 *Phys. Rev. Lett.* **1987**, *58*, 2059.
25
26
- 27 12. Liu, J.; Zhao, H.; Wu, M.; Van der Schueren, B.; Li, Y.; Deparis, O.; Ye, J.; Ozin, G. A.;
28 Hasan, T.; Su, B.-L. Slow Photons for Photocatalysis and Photovoltaics. *Adv. Mater.* **2017**, *29*,
29 1605349.
30
31
- 32 13. Guesh, K.; Márquez-Álvarez, C.; Chebude, Y.; Diaz, I. Enhanced Photocatalytic Activity
33 of Supported TiO₂ by Selective Surface Modification of Zeolite Y. *Appl. Surf. Sci.* **2016**, *378*,
34 473-478.
35
36
37
- 38 14. Wang, C.; Shi, H.; Li, Y. Synthesis and Characteristics of Natural Zeolite Supported Fe³⁺-
39 TiO₂ Photocatalysts. *Appl. Surf. Sci.* **2011**, *257*, 6873-6877.
40
41
42
- 43 15. Dong, H.; Zeng, G.; Tang, L.; Fan, C.; Zhang, C.; He, X.; He, Y. An Overview on
44 Limitations of TiO₂-Based Particles for Photocatalytic Degradation of Organic Pollutants and
45 the Corresponding Countermeasures. *Water Res.* **2015**, *79*, 128-146.
46
47
48
- 49 16. Zhu, X.; Chang, Y.; Chen, Y. Toxicity and Bioaccumulation of TiO₂ Nanoparticle
50 Aggregates in *Daphnia Magna*. *Chemosphere* **2010**, *78*, 209-215.
51
52
- 53 17. Hoffman, M. R.; Martin, S. T.; Choi, W.; Bahnemann, D. W. Environmental Applications
54 of Semiconductor Photocatalysis. *Chem. Rev.* **1995**, *95*, 69-96.
55
56
- 57 18. Chen, X.; Shen, S.; Guo, L.; Mao, S. S. Semiconductor-based Photocatalytic Hydrogen
58 Generation. *Chem. Rev.* **2010**, *110*, 6503-6570.
59
60

- 1
2
3 19. Liu, G.; Wang, L.; Yang, H. G.; Cheng, H.-M.; Lu, G. Q. Titania-Based Photocatalysts –
4 Crystal Growth, Doping and Heterostructuring. *J. Mater. Chem.* **2010**, *20*, 831-843.
5
6
7 20. Ollis, D. F.; Pelizzetti, E.; Serpone, N. Photocatalyzed Destruction of Water Contaminants.
8 *Environ. Sci. Technol.* **1991**, *25*, 1522-1529.
9
10
11 21. Liu, J.; Liu, G.; Li, M.; Shen, W.; Liu, Z.; Wang, J.; Zhao, J.; Jiang, L.; Song, Y.
12 Enhancement of Photochemical Hydrogen Evolution over Pt-Loaded Hierarchical Titania
13 Photonic Crystal. *Energy Environ. Sci.* **2010**, *3*, 1503-1506.
14
15
16
17 22. Kim, K.; Thiagarajan, P.; Ahn, H.-J.; Kim, S.-I.; Jang, J.-H. Optimization for Visible Light
18 Photocatalytic Water Splitting: Gold-Coated and Surface-Textured TiO₂ Inverse Opal Nano-
19 Networks. *Nanoscale* **2013**, *5*, 6254-6260.
20
21
22
23 23. Boppella, R.; Kochuveedu, S. T.; Kim, H.; Jeong, M. J.; Mota, F. M.; Park, J. H.; Kim, D.
24 H. Plasmon-Sensitized Graphene/TiO₂ Inverse Opal Nanostructures with Enhanced Charge
25 Collection Efficiency for Water Splitting. *ACS Appl. Mater. Interfaces* **2017**, *9*, 7075-7083.
26
27
28
29 24. Zhou, M.; Bao, J.; Xu, Y.; Zhang, J.; Xie, J.; Guan, M.; Wang, C.; Wen, L.; Lei, Y.; Xie,
30 Y. Photoelectrodes Based Upon Mo:BiVO₄ Inverse Opals for Photoelectrochemical Water
31 Splitting. *ACS Nano* **2014**, *8*, 7088-7098.
32
33
34
35 25. Sadakane, M.; Sasaki, K.; Kunioku, H.; Ohtani, B.; Abe, R.; Ueda, W. Preparation of 3-D
36 Ordered Macroporous Tungsten Oxides and Nano-Crystalline Particulate Tungsten Oxides
37 Using a Colloidal Crystal Template Method, and Their Structural Characterization and
38 Application as Photocatalysts under Visible Light Irradiation. *J. Mater. Chem.* **2010**, *20*, 1811-
39 1818.
40
41
42
43
44 26. Hirakawa, H.; Hashimoto, M.; Shiraishi, Y.; Hirai, T. Photocatalytic Conversion of
45 Nitrogen to Ammonia with Water on Surface Oxygen Vacancies of Titanium Dioxide. *J. Am.*
46 *Chem. Soc.* **2017**, *139*, 10929-10936.
47
48
49
50 27. Jiao, J.; Wei, Y.; Chi, K.; Zhao, Z.; Duan, A.; Liu, J.; Jiang, G.; Wang, Y.; Wang, X.; Han,
51 C.; Zheng, P. Platinum Nanoparticles Supported on TiO₂ Photonic Crystals as Highly Active
52 Photocatalyst for the Reduction of CO₂ in the Presence of Water. *Energy Technol.* **2017**, *5*,
53 877-883.
54
55
56
57 28. Ren, M.; Valsaraj, K. Inverse Opal Titania on Optical Fiber for the Photoreduction of CO₂
58 to CH₃OH. *Int. J. Chem. React. Eng.* **2009**, *7*, A90.
59
60

- 1
2
3 29. Fox, M. A.; Dulay, M. T. Heterogeneous Photocatalysis. *Chem Rev.* **1993**, *93*, 341-357.
4
5
6 30. Meng, S.; Li, D.; Wang, P.; Zheng, X.; Wang, J.; Chen, J.; Fang, J.; Fu, X. Probing Photonic
7 Effect on Photocatalytic Degradation of Dyes Based on 3D Inverse Opal ZnO Photonic Crystal.
8 *RSC Adv.* **2013**, *3*, 17021-17028.
9
10
11 31. Xie, H.; Li, Y.; Jin, S.; Han, J.; Zhao, X. Facile Fabrication of 3D-Ordered Macroporous
12 Nanocrystalline Iron Oxide Films with Highly Efficient Visible Light Induced Photocatalytic
13 Activity. *J. Phys. Chem. C* **2010**, *114*, 9706-9712.
14
15
16
17 32. Li, X.; Chen, Z.; Quan, H.; Shao, Y.; Li, D. Constructing Photocatalyst from β -Bi₂O₃
18 Photonic Crystals for Enhanced Photocatalytic Performance. *J. Porous Mater.* **2018**, *25*, 677-
19 685.
20
21
22
23 33. Curti, M.; Schneider, J.; Bahnemann, D. W.; Mendive, C. B. Inverse Opal Photonic Crystals
24 as a Strategy to Improve Photocatalysis: Underexplored Questions. *J. Phys. Chem. Lett.* **2015**,
25 *6*, 3903-3910.
26
27
28
29 34. Stein, A.; Wilson, B. E.; Rudisill, S. G. Design and Functionality of Colloidal-Crystal-
30 Templated Materials – Chemical Applications of Inverse Opals. *Chem. Soc. Rev.* **2013**, *42*,
31 2763-2803.
32
33
34
35 35. Gaillot, D. P.; Summers, C. J. Inverse Opal Photonics. In *Atomic Layer Deposition of*
36 *Nanostructured Materials*; Pinna, N., Knez, M., Eds.; Wiley-VCH: Weinheim, 2012; pp. 345-
37 371.
38
39
40
41 36. Likodimos, V. Photonic Crystal-Assisted Visible Light Activated TiO₂ Photocatalysis.
42 *Appl. Catal. B* **2018**, *230*, 269-303.
43
44
45 37. Zhai, C.; Zhu, M.; Lu, Y.; Ren, F.; Wang, C.; Du, Y.; Yang, P. Reduced Graphene Oxide
46 Modified Highly Ordered TiO₂ Nanotube Arrays Photoelectrode with Enhanced
47 Photoelectrocatalytic Performance under Visible-Light Irradiation. *Phys. Chem. Chem. Phys.*
48 **2014**, *16*, 14800-14807.
49
50
51
52 38. Liao, W.; Yang, J.; Zhou, H.; Murugananthan, M.; Zhang, Y. Electrochemically Self-
53 Doped TiO₂ Nanotube Arrays for Efficient Visible Light Photoelectrocatalytic Degradation of
54 Contaminants. *Electrochim. Acta* **2014**, *136*, 310-317.
55
56
57
58
59
60

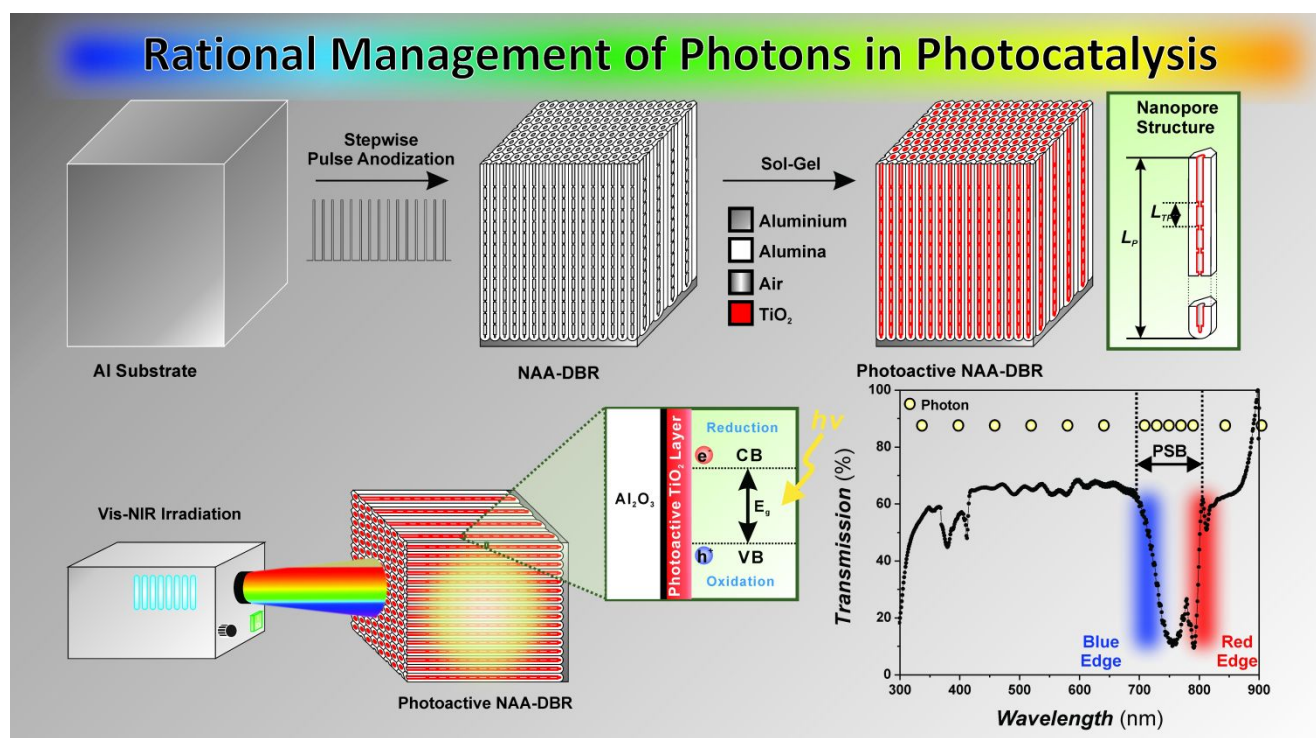
- 1
2
3 39. Wang, C.; Chen, D.; Ping, G. X.; Liu, S.; Huang, X. N.; Huang, Y. X.; Shu, K. Y.; Li, J. H.
4 Controllable Synthesis of Well-Ordered TiO₂ Nanotubes in a Mixed Organic Electrolyte for
5 High-Efficiency Photocatalysis. *Sci. China Chem.* **2012**, *55*, 2373-2380.
6
7
8
9 40. Mehedi, I. M.; Hossain, M. F.; Takahashi, T.; Islam, M. S. Nano-Structural Variation of
10 Highly Aligned Anodic Titania Nanotube Arrays for Gas Phase Photocatalytic Application. *J.*
11 *Photochem. Photobiol. A* **2017**, *335*, 200-210.
12
13
14
15 41. Santos, A.; Balderrama, V. S.; Alba, M.; Formentín, P.; Ferré-Borrull, J.; Pallarès, J.;
16 Marsal, L. F. Nanoporous Anodic Alumina Barcodes: Toward Smart Optical Biosensors. *Adv.*
17 *Mater.* **2012**, *24*, 1050-1054.
18
19
20
21 42. Law, C. S.; Sylvia, G. M.; Nemati, M.; Yu, J.; Losic, D.; Abell, A. D.; Santos, A.
22 Engineering of Surface Chemistry for Enhanced Sensitivity in Nanoporous Interferometric
23 Sensing Platforms. *ACS Appl. Mater. Interfaces* **2017**, *9*, 8929-8940.
24
25
26
27 43. Law, C. S.; Lim, S. Y.; Abell, A. D.; Santos, A. Real-Time Binding Monitoring between
28 Human Blood Proteins and Heavy Metal Ions in Nanoporous Anodic Alumina Photonic
29 Crystals. *Anal. Chem.* **2018**, *90*, 10039-10048.
30
31
32
33 44. Chen, Y.; Santos, A.; Wang, Y.; Kumeria, T.; Wang, C.; Li, J.; Losic, D. Interferometric
34 Nanoporous Anodic Alumina Photonic Coatings for Optical Sensing. *Nanoscale* **2015**, *7*, 7770-
35 7779.
36
37
38
39 45. Law, C.S.; Lim, S. Y.; Santos, A. On the Precise Tuning of Optical Filtering Features in
40 Nanoporous Anodic Alumina Distributed Bragg Reflectors. *Sci. Rep.* **2018**, *8*, 4642.
41
42
43
44 46. Santos, A.; Pereira, T.; Law, C. S.; Losic, D. Rational Engineering of Nanoporous Anodic
45 Alumina Optical Bandpass Filters. *Nanoscale* **2016**, *8*, 14846-14857.
46
47
48
49 47. Wang, Y.; Chen, Y.; Kumeria, T.; Ding, F.; Evdokiou, A.; Losic, D.; Santos, A. Facile
50 Synthesis of Optical Microcavities by a Rationally Designed Anodization Approach: Tailoring
51 Photonic Signals by Nanopore Structure. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9879-9888.
52
53
54
55 48. Law, C. S.; Lim, S. Y.; Abell, A. D.; Marsal, L. F.; Santos, A. Structural Tailoring of
56 Nanoporous Anodic Alumina Optical Microcavities for Enhanced Resonant Recirculation of
57 Light. *Nanoscale* **2018**, *10*, 14139-14152.
58
59
60

- 1
2
3 49. Chen, Y.; Santos, A.; Wang, Y.; Kumeria, T.; Ho, D.; Li, J.; Wang, C.; Losic, D. Rational
4 Design of Photonic Dust from Nanoporous Anodic Alumina Films: A Versatile Photonic
5 Nanotool for Visual Sensing. *Sci. Rep.* **2015**, *5*, 12893.
6
7
8
9 50. Sukarno; Law, C. S.; Santos, A. Realisation and Optical Engineering of Linear Variable
10 Bandpass Filters in Nanoporous Anodic Alumina Photonic Crystals. *Nanoscale* **2017**, *9*, 7541-
11 7550.
12
13
14
15 51. Santos, A.; Yoo, J. H.; Rohatgi, C. V.; Kumeria, T.; Wang, Y.; Losic, D. Realisation an
16 Advanced Engineering of True Optical Rugate Filters Based on Nanoporous Anodic Alumina
17 by Sinusoidal Pulse Anodisation. *Nanoscale* **2016**, *8*, 1360-1373.
18
19
20
21 52. Lim, S. Y.; Law, C. S.; Marsal, L. F.; Santos, A. Engineering of Hybrid Nanoporous Anodic
22 Alumina Photonic Crystals by Heterogeneous Pulse Anodization. *Sci. Rep.* **2018**, *8*, 9455.
23
24
25 53. Abràmoff, M. D.; Magalhães, P. J.; Ram, S. J. Image Processing with ImageJ. *Biophotonics*
26 *Inter.* **2004**, *11*, 36-42.
27
28
29 54. Nishimura, S.; Abrams, N.; Lewis, B. A.; Halaoui, L. I.; Malluok, T. E.; Benkstein, K.D.;
30 van de Lagemaat, J.; Frank, A. J. Standing Wave Enhancement of Red Absorbance and
31 Photocurrent in Dye-Sensitized Titanium Dioxide Photoelectrodes Coupled To Photonic
32 Crystals. *J. Am. Chem. Soc.* **2003**, *125*, 6306-6310.
33
34
35
36 55. Li, Y.; Kunitake, T.; Fujikawa, S. Efficient Fabrication and Enhanced Photocatalytic
37 Activities of 3D-Ordered Films of Titania Hollow Spheres. *J. Phys. Chem. B* **2006**, *110*, 13000-
38 13004.
39
40
41
42 56. Deparis, O.; Mouchet, S. R.; Su, B.-L. Light Harvesting in Photonic Crystals Revisited:
43 Why do Slow Photons at the Blue Edge Enhance Absorption? *Phys. Chem. Chem. Phys.* **2015**,
44 *17*, 30525-30532.
45
46
47
48 57. Brzózka, A.; Brudzisz, A.; Hnida, K.; Sulka, G. D. Chemical and Structural Modifications
49 of Nanoporous Alumina and Its Optical Properties. In *Electrochemically Engineered*
50 *Nanoporous Materials: Methods, Properties and Applications*; Losic, D., Santos, A., Eds.;
51 Springer International Publishing: Cham, 2015; Vol. 220, pp. 219-288.
52
53
54
55 58. Kim, S.; Choi, W. Visible-Light-Induced Photocatalytic Degradation of 4-Chlorophenol
56 and Phenolic Compounds in Aqueous Suspension of Pure Titania: Demonstrating the
57 Existence of a Surface-Complex-Mediated Path. *J. Phys. Chem. B* **2005**, *109*, 5143-5149.
58
59
60

59. Lee, K.; Mazare, A.; Schmuki, P. One-Dimensional Titanium Dioxide Nanomaterials: Nanotubes. *Chem. Rev.* **2014**, *114*, 9385-9454.

60. Lettmann, C.; Hildenbrand, K.; Kisch, H.; Macyk, W.; Maier, W.F. Visible Light Photodegradation of 4-Chlorophenol with a Coke-Containing Titanium Dioxide Photocatalyst. *Appl. Catal. B* **2001**, *32*, 215-227.

TABLE OF CONTENTS



1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
26
27
28
29
30
31
32
33
34
35
36
37
38
39
40
41
42
43
44
45
46
47
48
49
50
51
52
53
54
55
56
57
58
59
60