Article

Tailoring Black TiO_2 Thin Films: Insights from Hollow Cathode Hydrogen Plasma Treatment Duration

Armstrong Godoy-Junior [1,*], André Pereira [1], Barbara Damasceno [1], Isabela Horta [1], Marcilene Gomes [2], Douglas Leite [1], Walter Miyakawa [3], Maurício Baldan [4], Marcos Massi [5], Rodrigo Pessoa [1,*] and Argemiro da Silva Sobrinho [1,*]

[1] Laboratório de Plasmas e Processos-LPP, Instituto Tecnológico de Aeronáutica–ITA, Praça Mal. Eduardo Gomes, 50, São José dos Campos/SP, 12228-900, Brazil; andreljpereira@gmail.com (A.P.); barbdara@gmail.com (B.D.); isabelah1@poli.ufrj.br (I.H.); leite@ita.br (D.L.)
[2] Instituto Federal de Educação, Ciência e Tecnologia de São Paulo–IFSP, Rod. Pres. Dutra, km 145, São José dos Campos/SP, 12223-201, Brazil; marcilenecgomes@ifsp.edu.br
[3] Instituto de Estudos Avançados–IEAv, Trevo Coronel Aviador José Alberto Albano do Amarante, 1, São José dos Campos/SP, 12228-001, Brazil; walter.toshi@gmail.com (W.M.)
[4] Instituto Nacional de Pesquisas Espaciais–INPE, Av. dos Astronautas, 1758, Jardim da Granja, São José dos Campos/SP, 12227-010, Brazil; mrbaldan@gmail.com
[5] Escola de Engenharia, Universidade Presbiteriana Mackenzie, Consolação, 930, São Paulo/SP, 01302-907, Brazil; massi.marcos@gmail.com
* Correspondence: godoyajr@gmail.com (A.G.-J.); rspessoa@ita.br (R.P.); argemiro@ita.br (A.d.S.S.)

Material and Methods

Pristine Anatase TiO_2 Thin Films Growth

Pristine TiO_2 thin films with 300–400 nm thick were grown onto pieces of glass and Si (100) using a DC reactive magnetron sputtering system with a circular Ti target (34 mm diameter) [29]. The Ti target was sputtered in Ar plasma for 10 min before the deposition for cleaning purposes. The cylindrical deposition chamber was backfilled with a flow of 15 sccm and 3 sccm of Ar and O_2 gases, respectively. The Ti target was powered with 150 W by the Advanced Energy (MDX 1K) DC power supply and the target-to-substrate distance was set at 30 mm. The deposition process lasted 30 min and the chamber was evacuated by a diffusion pump (Edwards – CR63/150 Diffstak-230 1/s) serially connected with a mechanical pump (Edwards – E2M18) providing a residual and work pressures of 4×10^{-3} Pa (3×10^{-5} Torr) and 1.3 Pa (1×10^{-2} Torr), respectively. The thin films were deposited at room temperature (RT) but after 30 min of deposition, the temperature measured in the substrate holder reached ~100 °C.

Hydrogenation Process

Firstly, the pristine anatase TiO_2 thin films were placed inside the hollow cathode, which was positioned over the chamber electrode. The working and residual pressures were 13.3 Pa (1×10^{-1} Torr) and 5.0×10^{-1} Pa (4×10^{-3} Torr), respectively. Before generating the H_2 plasma, the chamber was purged with H_2 gas for 5 min. The H_2 plasma was ignited and sustained at 200 W with a bias voltage of ~380 V by an RF power supply (Kurt J. Lesker, R601 13.56 MHz) under the H_2 gas atmosphere with a flow of 45 sccm. The hollow cathode wall temperature was monitored and reached the maximum temperature of approximately 260 °C after 8 min and remained constant during the hydrogenation process. For more details of the system see reference [11].

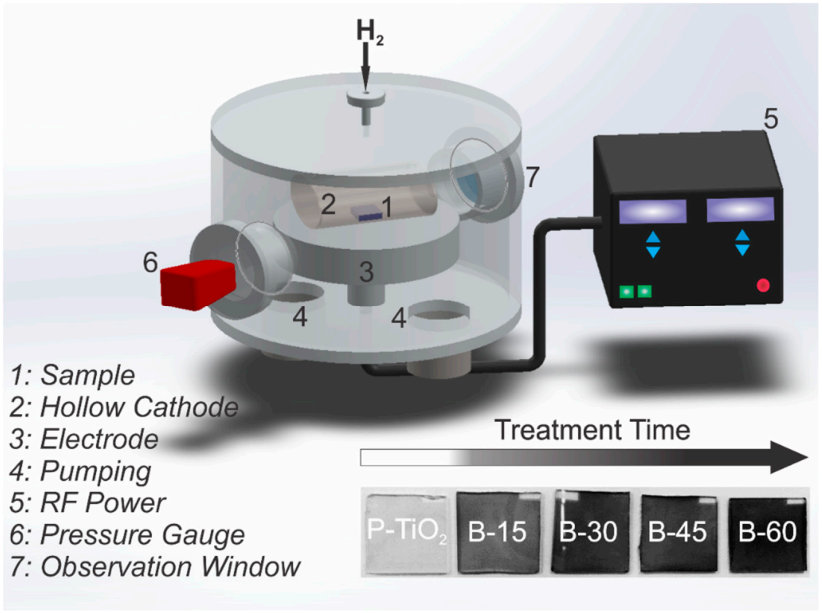

Figure S1. Schematic of the hollow cathode hydrogen plasma (HCHP) system used for the pristine anatase TiO_2 thin films hydrogenation. The lower right side presents photographs of the samples before and after the HCHP process for 15, 30, 45, and 60 minutes.

Photocatalytic Activity Evaluation

The photocatalytic degradation experiments were conducted in a homemade reactor equipped with 6 UV-visible germicide lamps with 15 W (Osram, model HNS G13-G15T8/OF) air-cooled. A schematic diagram showing the details of the system are shown in **Figure S2.** The lamps were fixed at 70 mm away from the samples, which present an active area of 2 × 2 cm^2, delivering an irradiance of 2.2 mW cm^{-2} at the sample position [31,32]. Noteworthy that the main lamp emission peak (250 nm) is not detected by the reference cell, thus the irradiance can be higher than the value reported (See **Figure S3**). A becker equipped with a water jacket system was used in all experiments to maintain the solution at RT. The photocatalytic degradation of MB was carried out at atmospheric conditions (25 ºC). In a typical experiment, pristine and black TiO_2 thin films deposited on glass substrates were placed into a 6 mL aqueous solution of MB (10 $mg.L^{-1}$) separately. Each mixture was magnetically stirred during the photocatalytic process. Before the UV irradiation, the solution was held in dark for 1 h to establish the adsorption/desorption equilibrium conditions between the MB dye and the surfaces of the films. Later, the lamps were turned on. The systems were continuously stirred during all the processes. The MB degradation was measured every 10 min by the UV-Vis spectrophotometer (ThermoFischer Scientific, model Evolution 220).

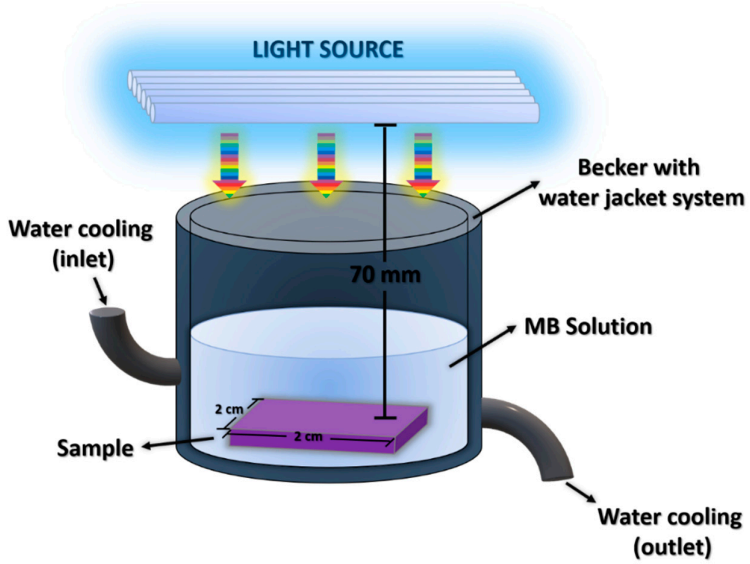

Figure S2. Schematic diagram of the photocatalysis homemade system used for the photocatalytic activity evaluation.

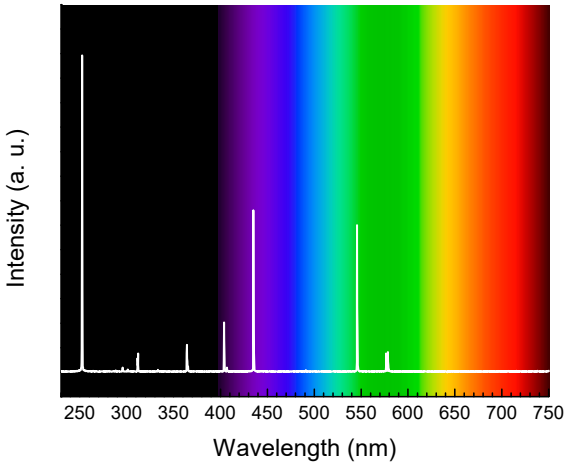

Figure S3. Emission spectrum of germicide lamp UV-Vis radiation used in the photocatalytic assays.

Reference

[29] Duarte, D.A.; Massi, M.; Da Silva Sobrinho, A.S. Comparison between Conventional and Hollow Cathode Magnetron Sputtering Systems on the Growing of Titanium Dioxide Thin Films: A Correlation between the Gas Discharge and Film Formation. *EPJ Appl. Phys.* **2011**, *54*, 20801. https://doi.org/10.1051/epjap/2011100453.

[11] Godoy, A., Jr.; Pereira, A.; Gomes, M.; Fraga, M.; Pessoa, R.; Leite, D.; Petraconi, G.; Nogueira, A.; Wender, H.; Miyakawa, W.; et al. Black TiO_2 Thin Films Production Using Hollow Cathode Hydrogen Plasma Treatment: Synthesis, Material Characteristics and Photocatalytic Activity. *Catalysts* **2020**, *10*, 282. https://doi.org/10.3390/catal10030282.

[31] Gomes, L.E.; Da Silva, M.F.; Gonçalves, R.V.; Machado, G.; Alcantara, G.B.; Caires, A.R.L.; Wender, H. Synthesis and Visible-Light-Driven Photocatalytic Activity of Ta^{4+} Self-Doped Gray Ta_2O_5 Nanoparticles. *J. Phys. Chem. C* **2018**, *122*, 6014–6025. https://doi.org/10.1021/acs.jpcc.7b11822.

[32] Nogueira, A.C.; Gomes, L.E.; Ferencz, J.A.P.; Rodrigues, J.E.F.S.; Gonçalves, R.V.; Wender, H. Improved Visible Light Photoactivity of $CuBi_2O_4$/CuO Heterojunctions for Photodegradation of Methylene Blue and Metronidazole. *J. Phys. Chem. C* **2019**, *123*, 25680–25690. https://doi.org/10.1021/acs.jpcc.9b06907.