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Highly Ordered TiO_2-WO_3 Modified Nanotubes Array for Photoelectrocatalytic Oxidation of Methyl Orange

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Coupled titanium dioxide-tungsten oxide array surface was used to remove methyl orange from water by photocatalytic anodic oxidation. The coating was prepared by anodizing a titanium foil in a glycerol/water electrolyte-containing NH_4F followed by thermal treatment. Moreover, subsequent WO_3 electrodeposition was realized on the previously obtained TiO_2 nanotubular structure. As comparison, TiO_2-WO_3 structures were obtained by adding a tungstate salt in the glycerol/water electrolyte during the anodization step of Ti foil. Scanning electron microscopy imaging showed that the array coating consisted of closely spaced nanotubes perpendicular to the titanium plate. Moreover, subsequent electrodeposition of WO_3 occurred on the wall of the nanotubes; when a tungstate salt was used during Ti anodization, the formation of nanotubes with different dimensions was observed.

The synthesized materials were studied for the photoelectrocatalytic oxidation of methyl orange under applied bias potential. The degradation efficiency obtained using TiO_2 nanotubes was higher than that obtained in presence of the coupled structure.

1. Introduction

The growth of water pollution by organic compounds from textile, cosmetic, pharmaceutical industries, agriculture and urban activities is one of the main current worldwide concern. The most common recalcitrant organic pollutants are dyes, chemicals, and drugs, that are currently discharged in effluents and introduced in the aquatic environment (Brillas and Martinez-Huitle, 2015).

Textile dyes take a long time to degrade under natural conditions. Moreover, many of these dyes are mutagenic and carcinogenic, causing substantial injury to human life (Cañizares et al., 2006).

Depending on the nature and the concentration of pollutants, different wastewaters treatments have been proposed, such as physicochemical, biological, and chemical methods (Forgacs et al., 2004; Van der Zee and Villaverde, 2005; Santos et al., 2007; Mais et al., 2016). However, the main drawback of these methods is the incomplete degradation of the pollutants, that cause secondary pollution problems.

Among the possible advanced oxidation process (AOP), photocatalysis can be considered as an effective method to completely degrade the dye molecules (Li et al., 2006; Oturan and Aaron, 2014). Moreover, photoelectrocatalysis (PEC) has deserved increasing attention in the last decades as a new technology to degrade complex pollutant efficiently (Brillas and Gargia Segura, 2017). In this process a semiconductor photoanode is irradiated by light with energy equal to or greater than its band gap, while a bias potential is contemporary applied, to decrease recombination driving the photogenerated charges through the external circuit. With respect to different electrochemical methods used to decontaminate wastewaters containing organic dyes, photoelectrochemical processes show high efficiency, especially when they are carried out under solar energy (Karanasios et al., 2015). In PEC processes, the degradation rate of organic pollutants depends, to some extent, on the activity of the photoanode; therefore, improving its activity has become a primary research focus (Ampudia et al., 2016).

The anatase crystalline form of TiO_2 is the material more extensively used as photoanode in PEC applications, due to its low cost, low toxicity and high stability with a band gap value of 3.2 eV. WO_3 is also a n-type

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semiconductor metal oxide, with a band gap value around 2.5 and 2.7 eV, which is lower than that of TiO_2; for this reason, WO_3 presents better performance under visible light irradiation (Reyes-Gil and Robinson, 2013).

In this study, methyl orange, ($C_{14}H_{14}N_3NaO_3S$) a colored compound used in dyeing and printing textiles, was used as a model organic dye to be removed from wastewaters, in a batch reactor, by photoelectrocatalytic oxidation on TiO_2 and TiO_2-WO_3 combined structures.

Li et al. reported that the high degradation rates of methyl orange dye in wastewaters can be obtained using TiO_2-coated activated carbon. The authors highlighted that the organic substances are oxidized on the photocatalytic surface, and the reaction intermediates are adsorbed and further oxidized, preventing secondary pollution by the intermediates (Li et al., 2006).

Martin de Vidales et al. used methyl orange as a model organic dye to be removed from wastewaters by PEC oxidation on TiO_2 photoanode in a flowing electrolyte cell. At higher flow rates the process efficiency was higher, due to the removal of the oxidation products from the electrode surface, observing a fast discoloration of the solution (Martin de Vidales et al., 2016).

Nanoporous WO_3 photoanodes have been fabricated by electrochemical anodization of tungsten foil and used as catalyst for photoelectrocatalytic oxidation of methyl orange under visible irradiation (Zheng and Lee, 2014). The experimental results revealed that the dye was efficiently removed, and the simultaneous mineralization was achieved in the adopted conditions.

In the present work we investigated the use of TiO_2 nanotubes as a skeleton to develop WO_3/TiO_2 nanostructures. Nanostructured WO_3/TiO_2 composites have been prepared following two different steps: anodization of Ti foils was performed first to obtain the TiO_2 nanotubular structures (NTs), and then the electrodeposition of WO_3 was realized on NTs using pulse potential techniques. Moreover, a tungstate salt was added to the anodization bath; in this case TiO_2-WO_3 systems have been obtained by one-step anodization of Ti foil, in which the tungsten oxide phase was in direct contact with the Ti conductive layer.

Depending on the experimental conditions, different morphologies of the deposit were obtained and in turn, different performances were measured in terms of photocurrent responses at the related samples.

2. Materials and methods

2.1 Synthesis of nanostructured electrodes: TiO_2 and TiO_2/WO_3 nanotubes

Electrochemical oxidation technique was used to obtain the TiO_2 nanotubular structure starting from Ti foils (0.25 mm thickness, 99.7 % metal basis, Aldrich), that were used as raw materials. Prior to the electrochemical oxidation, Ti foils were degreased by sonication, for 10 minutes in each solvent, in acetone, then in isopropanol and finally in methanol; then, they were rinsed with deionized water and dried in a Nitrogen stream. The electrolytic solution used for the oxidation process of Ti foil was composed by (10%) deionized water / (90%) glycerol organic solution with 0.14 M of NH_4F at room temperature. A potential ramp was imposed from open circuit voltage (OCV) at a fixed potential of 20 V with a scan rate of 100 mVs^{-1}. The applied potential was maintained at this fixed value for 4 h. A final annealing treatment was required in order to transform the amorphous structure into a crystalline one and it was performed in air atmosphere at 400°C for 1 h.

In order to obtain TiO_2/WO_3 nanotubular structures, two different techniques were employed. In the first case the TiO_2/WO_3 nanotubular structures were prepared by one-step electrochemical oxidation of Ti foil, as previously explained, in a mixture electrolyte containing 12 mM of $Na_2WO_4 \cdot 2H_2O$ (TiO_2/W in the rest of the text). In the second case, the electrodeposition of tungsten oxide was performed at room temperature in a classical three-electrode cell in which a saturated calomel electrode (SCE) was the reference, a platinum grid was the counter electrode, while titania was used as working electrode, as explained in a previous work (Palmas et al., 2016) (TiO_2/Wy, y indicating the deposition time in seconds, in the rest of the text). The obtained TiO_2/WO_3 samples were annealed in air atmosphere at 400°C for 2h.

2.2 Characterization of samples

The surface morphology of the deposited films was investigated by high resolution Scanning Electron Microscope (SEM) equipped with Energy Dispersive X-Ray (EDX) detector (Zeiss, Germany). Top views of the TiO_2 nanotubes were taken before and after WO_3 eletrodeposition.

A three-electrode cell with a quartz window equipped by a Pt-grid counter electrode and a SCE reference was used for all photoelectrochemical studies. Photoanodes were irradiated simultaneously by UV-vis light: photocurrent measurements were performed using a 300W xenon lamp equipped with air mass (AM) 0 and 1.5 D filters, which were used to simulate the solar irradiation.

Electrochemical measurements were recorded using a potentiostat-galvanostat (Amel 7050), controlled by Junior Assist software.

2.3 Experimental details

The laboratory-scale electrolysis was carried out with 20 cm^3 solution containing 0.25 mM of methyl orange (MO) in 0.1 M Na_2SO_4 supporting electrolyte (pH solution=6.5) at a constant potential of 1.75V vs. SCE. Na_2SO_4 was selected as an inert supporting electrolyte, since it has no effect on the electrolyte products.

The absorbance of the selected samples, taken at regular time intervals during photoelectrocatalysis of the MO solution, was measured by UV/visible spectroscopy (Agilent Technologies Cary Series Spectrophotometer) at an absorption wavelength of 465 nm.

3. Results and discussion

Figure 1 shows the morphology of the photoelectrodes; in particular, TiO_2 nanotubes (Figure 1a) are highly uniform and vertically oriented with a diameter of 50 nm of average size. When the electrochemical anodization of the Ti foil is conducted in presence of 12 mM of tungstate salt, the formation of nanotubes with different dimensions can be observed (Figure 1b). Moreover, higher diameters of the pores and a decrease in the definition of the circular shape of the pore were observed at higher sodium tungstate concentration values (data not reported).

After the electrodeposition process of tungsten oxide on the TiO_2 surface, WO_3 tubular nanostructures grew on top of the TiO_2 nanotubes: at the beginning of the electrodeposition process (5 s), the WO_3 particles seem to be deposited around the walls of the TiO_2 nanotubes (Figure 1c). After 10 s of deposition, the SEM analysis (Figure 1d) indicates that at the TiO_2/W10 sample the nanotubular structure is still evident, deposition of WO_3 occurring mostly at the walls of tubes. Moreover, longer deposition times generate a cracked compact layer of WO_3 at the top of the nanotubes (data not reported).

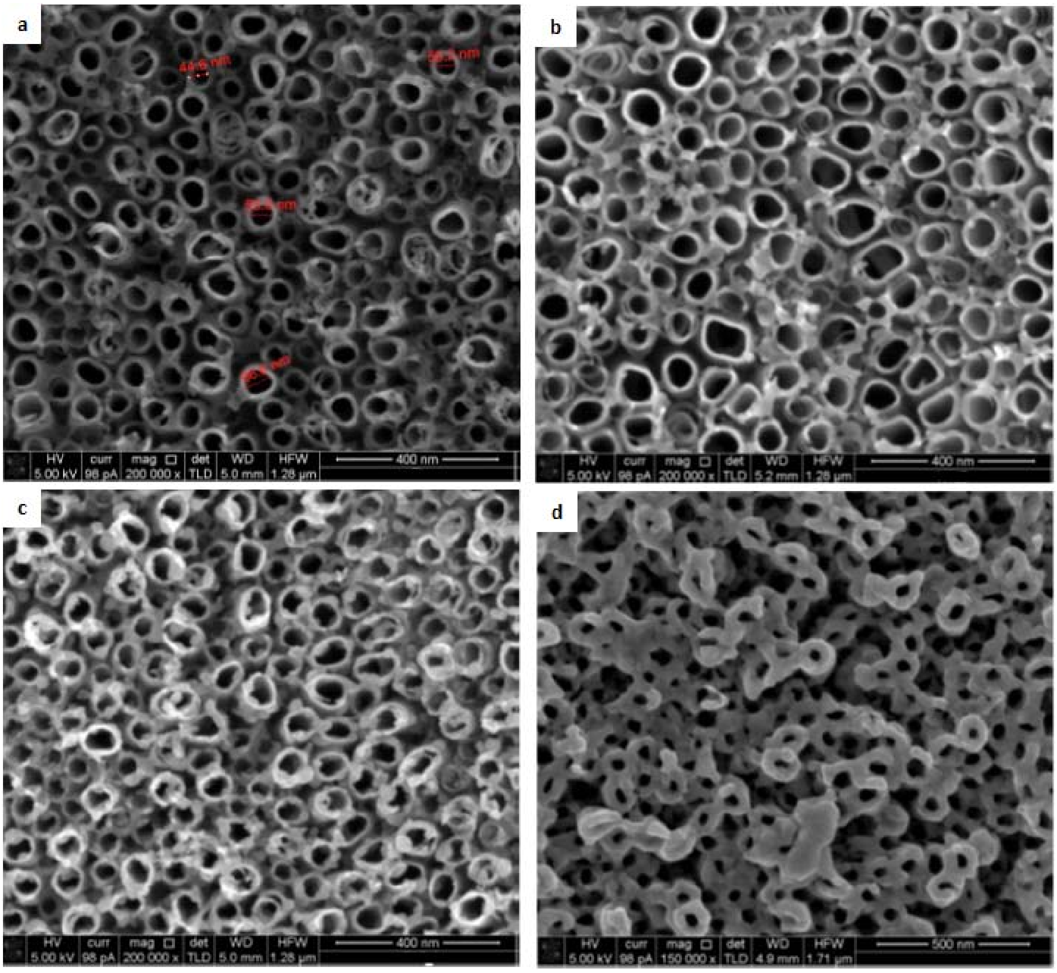

Figure 1: SEM micrographs of synthesized sample TiO_2 (a), TiO_2-W (b), TiO_2-W5 (c) and (d) TiO_2-W10 electrodes.

As observed in a previous study (Palmas et al., 2016), higher WO_3 loading corresponds to a negative effect on the photocatalytic response, which could be due either to an increase in the charge recombination, or to a decrease in the specific area of the electrode: plugging of nanotubes by tungsten oxide could reduce the TiO_2/electrolyte interface.

In order to test the photocatalytic activity of the synthesised samples, linear sweep voltammetries were performed in presence and absence of 0.25 mM MO in 0.1 M Na_2SO_4 both under UV-Vis light and dark conditions at a potential sweep rate of 10 mV/s starting from the open circuit potential to 2 V vs SCE.

Figure 2 reports, as an example, the results obtained using TiO_2 nanotubes as working electrode. The current recorded under UV-Vis light in absence of MO corresponds to the photocatalytic current generated by the TiO_2 nanotubes on the anode. The LSV, recorded in presence of MO under UV-Vis light, shows higher current values, indicating the catalytic activity of TiO_2 nanotubes for MO oxidation. Photocurrent became negligible under dark conditions, which suggests that the TiO_2 nanotubes alone are not catalytic towards the oxidation of MO.

In fact, the light allows the generation of e^-_{cb}/h^+_{vb} pairs: photogenerated h^+_{vb} is a strong oxidizing specie that is able to oxidize organic pollutants up to their complete mineralization. Literature work also proposed the reaction of h^+_{vb} with adsorbed water to form the strong oxidant $^{\bullet}OH$ which mineralize the organic pollutant, although there is no clear evidence for the formation of free hydroxyl radical from h^+_{vb} (Brillas and Gargia Segura, 2017).

The results obtained from LSV analysis indicate that the removal of MO via the photoelectrocatalytic oxidation can be carried out at constant potential electrolysis between 0.5 V and 2 V vs. SCE.

Higher positive potential values could destroy the structure and conductivity of titanium dioxide nanotubes (Roy et al., 2011); moreover, if the bias potential is set at values higher than 2 V, intense reactions of oxygen evolution occurs.

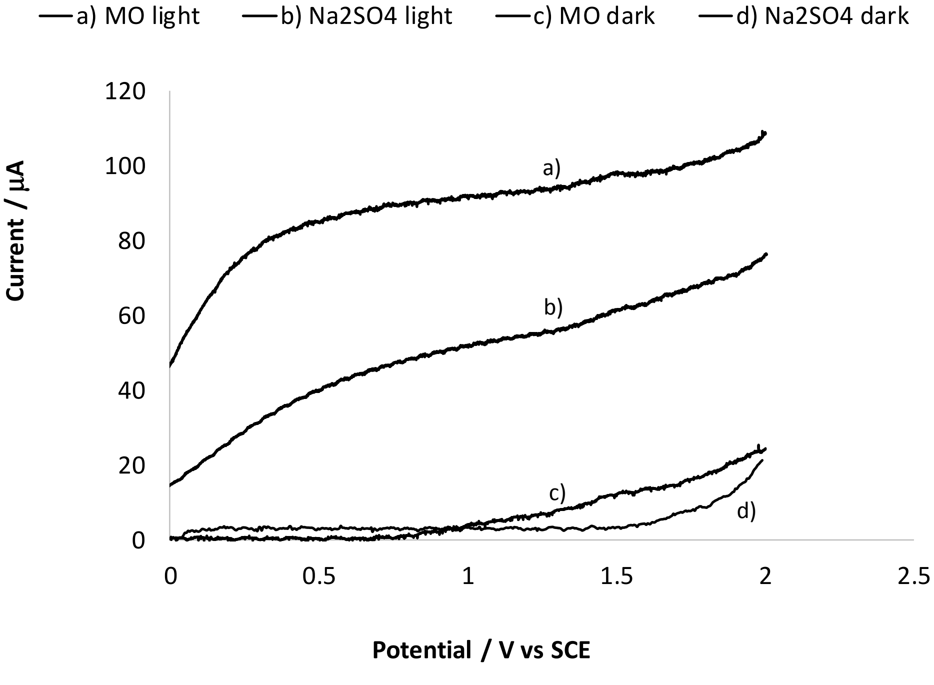

Figure 2: Voltammetric study of the influence of pollutant and UV-Vis light irradiation. [MO]=0.25 mM, [Na_2SO_4]=0.1 M. Working electrode being TiO_2 nanotubes; potential sweep rate 10 mV/s.

In order to study the photoelectrocatalytical removal MO, solutions containing 0.25 mM MO in 0.1 M Na_2SO_4 at pH 6.5 have been electrolyzed at a potential value of 1.75 V vs SCE. Figure 3 compares the MO removal over reaction time for the four different electrodes; the extent of methyl orange degradation with the bare TiO_2 nanotubes is higher respect to TiO_2-WO_3 combined structure.

In fact, at the TiO_2 electrode the abatement recorded after 7h reached approximately 70%, whereas with theTiO_2-WO_3 supports, the electrode reached the maximum degradation value of 33% for both TiO_2-W10 and TiO_2-W electrodes. When TiO_2-W5 is used as working electrode, the percent MO degradation after 7h was 60%.

It is worth to noticed that TiO2 and WO_3 semiconductor have different band gap values, 3.2 eV and 2.8 eV, respectively. The relatively low band gap value of WO_3 extends the photoresponse of this material into the visible wavelength range, much more than for TiO_2. As reported in a previous work (Palmas et al., 2016), if the TiO_2/WO_3 structures are irradiated at a fixed wavelength in the UV and near-visible range, higher photocatalytic responses are obtained when TiO_2 is coupled with WO_3.

When the electrode is irradiated by solar light, as in the present work, a different behaviour is observed, TiO_2 nanotubes becoming more effective for pollutants degradation.

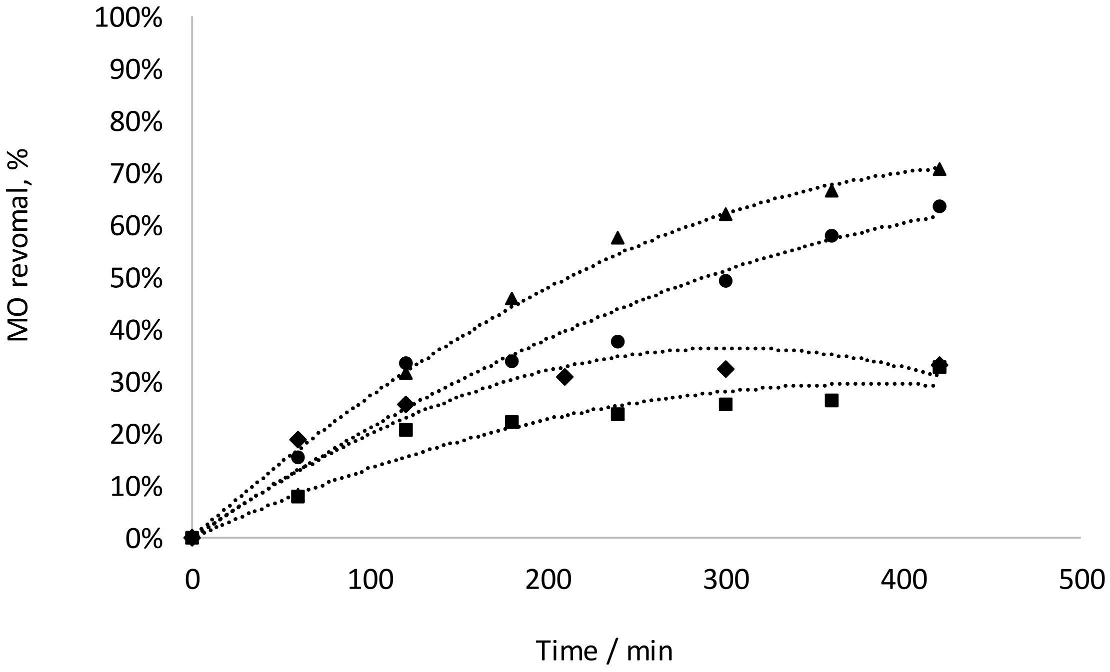

Figure 3: Effect of the working electrode material used for the oxidation of methyl orange under UV-Vis light. [MO]=0.25 mM, [Na_2SO_4]=0.1 M. Electrode potential = 1.75V vs SCE. (▲) TiO_2, (■) TiO_2/W, (●) TiO_2/W5, (♦) TiO_2/W10.

The faster MO degradation was achieved when both the light irradiation and the bias potential were applied in the photocatalytic process; in fact, the oxidation percentage achieved in photoelectrocatalysis is higher than for photocatalytic and electrocatalytic processes, according to the results obtained in our laboratories at the same anodic materials (data not shown).

4. Conclusions

In this work, TiO_2 nanotubes and coupled TiO_2/WO_3 nanostructures have been synthesised by using electrochemical methods.

The degradation of a model organic compound (methyl orange) has been performed using the prepared structures by applying both a bias potential and a light irradiation.

The synthesis of a TiO_2 nanotubular array by anodizing in a NH_4F electrolyte allows efficient oxidation of MO from synthetic wastewater by photoelectrocatalytic degradation, reaching the maximum value of 70%.

When coupled TiO_2/WO_3 nanostructures are used, lower degradation values have been recorded, depending on the WO_3 amount on the TiO_2 nanotubes.

Reference

Ampudia P., Palmas S., Vacca A., Mascia M., Mais L., Marken F., 2016, Mixed oxides for photo-electrochemical applications, Chem. Eng. Trans. 47, 145-150.

Brillas E., Gargia-Segura S., 2017, Applied photoelectrocatalysis on the degradation of organic pollutants in wastewaters, J. Photochem. Photobiol. C: Photochem. reviews, 31, 1-35.

Brillas E., Martinez-Huitle C.A., 2015, Decontamination of wastewaters containing synthetic organic dyes by electrochemical methods. An updated review, Appl. Catal. B: Environm. 166, 603-643.

Cañizares P., Martínez F., Jiménez C., Lobato J., Rodrigo M.A., 2006, Coagulation and Electrocoagulation of Wastes Polluted with Dyes, Environ. Sci. Technol. 40, 6418–6424.

Forgacs E, Cserhati T and Oros G, 2004, Removal of synthetic dyes from wastewaters: a review, Environ. Int. 30, 953-971.

Karanasios N., Georgieva J., Valova E., Armyanov S., Litsardakis G., Sotiropoulos S., 2015, Photoelectrocatalytic Oxidation of Organics Under Visible Light Illumination: A Short Review, Curr. Org. Chem. 19, 512-520.

Li Y., Li X., Li J., Yin J., 2006, Photocatalytic degradation of methyl orange by TiO2-coated activated carbon and kinetic study, Water Res. 40, 1119-1126.

Mais L., Ampudia P., Palmas S., Vacca A., Mascia M., Ferrara F., 2016, Synthesis of nanostructured materials for photoelectrochemical oxidation of organic compounds, Chem. Eng. Trans. 47, 157-162.

Martin de Vidales M.J., Mais L., Saez C., Canizares P., Walsh F.C., Rodrigo M.A., De Arruda Rodrigues C., Ponce de Leon C., 2016, Photoelectrocatalytic Oxidation of Methyl Orange on a TiO2 Nanotubular Anode Using a Flow Cell, Chem. Eng. Technol. 39, 135-141.

Oturan M.A., Aaron J.J., 2014, Advanced oxidation processes in water/wastewater treatment: principles and applications. A review, Crit. Rev. Environ. Sci. Technol. 44, 2577-2641.

Palmas, S., Castresana, P.A., Mais, L., Vacca, A., Mascia, M., Ricci, P.C., 2016, TiO2/WO3 nanostructured systems for photoelectrochemical applications, RSC Adv. 6, 101671-101682.

Reyes-Gil K. R., Robinson D.B., 2013, WO_3-enhanced TiO_2 nanotube photoanodes for solar water splitting with simultaneous wastewater treatment, Appl. Mater. Interf. 5, 12400-12410.

Roy P., Berger S., Schmuki P., 2011, TiO2 nanotubes: synthesis and applications, Angew Chem. Int. Ed. Engl. 50, 2904-2939.

Santos A.B., Cervantes F.J., Lier J.B.V., 2007, Review paper on current technologies for decolourisation of textile wastewaters: perspectives for anaerobic biotechnology, Biores. Technol. 98, 2369-2385.

Van der Zee F.P., Villaverde S., 2005, Combined anaerobic-aerobic treatment of azo dyes - a short review of bioreactor studies, Water Res. 39, 1425-1440.

Zheng Q., Lee C., 2014, Visible light photoelectrocatalytic degradation of methyl orange using anodized nanoporous WO3, Electrochim. Acta 115, 140-145.