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Fe-modified TiO_2 Nanotube Layer as a Photochemically Versatile Material for the Degradation of Organic Pollutants in Water †

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† Presented at the 1st International Electronic Conference on Processes: Processes System Innovation, 17–31 May 2022; Available online: https://ecp2022.sciforum.net.

Citation: Lastname, F.; Lastname, F.; Lastname, F. Title. *Proceedings* **2022**, *69*, x. https://doi.org/10.3390/xxxxx

Academic Editor: Firstname Lastname

Published: date

Abstract: TiO_2 nanotube layers (TNT) are prepared by electrochemical anodization of Ti foil in an electrolyte composed of ethylene glycol, ammonium fluoride, and water. The surface of TNT is modified by iron using spin-coating of $Fe(NO_3)_3$/IPA (isopropyl alcohol) solution of different concentrations (10μM-100mM). The as-prepared materials are annealed at 450 °C for 2 h to form crystalline Fe-TNT. The phase identification and surface morphology of the materials are investigated by XRD and SEM/EDX, respectively. The novelty of this work is based on the investigation of different photochemical processes that could occur simultaneously, and it includes mainly photocatalysis and Fenton-based processes since iron is a Fenton-active element. To this end, the degradation of caffeine, an organic pollutant, is performed under solar-like radiation at pH = 3 using different systems that are Fe-TNT material alone, a radical precursor alone (H_2O_2 = 1mM), and Fe-TNT combined with H_2O_2. It is worth noting the degradation mechanism of the organic pollutants occurs via advanced oxidation processes where hydroxyl radicals have been identified as the main reactive oxygen species. One of the main goals of this work is to determine the contribution of the different involved photochemical processes (photocatalysis, photo-Fenton, and photolysis) along with the potential synergy between all these processes. To resume, this work provides new insights into the concept of photochemical versatility, which is scarcely described in the literature.

Keywords: nanotube, photocatalysis; Fenton; synergy; pollutant; water

1. Introduction

Water plays a vital role for all living beings. Although one third of the Earth's surface is covered with water, only 3% is consumable, out of which <1% is accessible [1]. The anthropogenic activities, especially those from industries, increase the rate of pollutants in the natural environment by releasing treated wastewaters that are not efficiently cleaned. Therefore, persistent and emerging organic pollutants including toxic chemicals, pharmaceutical compounds, pesticides, etc. are accumulated in the environment thus causing harmful diseases not only to mankind but also to the ecosystem [2]. It is the case of caffeine which is one of the most used psychoactive substance and which is often detected in natural waters [3]. It is essential to look for efficient wastewater treatment. Advanced oxidation processes (AOPs) have become an alternative technology for efficiently removing persistent organic pollutants from the water due to the generation of highly reactive inorganic radicals, including •OH, that oxidize and mineralize the pollutants [4]. Among the various AOPs, the photocatalysis and the Fenton-based processes are promising due to their low cost, ambient reaction conditions, and easy operation procedures. In photocatalysis, a semiconductor photocatalyst can generate electron (e^-) and hole (h^+) pairs (Equation 1), which in turn forms reactive oxygen species (ROS) such as $O_2^{\bullet-}$ and •OH (Equation 2 and 3), under light irradiation with energy higher than the photocatalyst energy bandgap (E_g) [5,6]. The Fenton and photo-Fenton process is based on the generation of •OH in the presence of Fe(III), H_2O_2, and light irradiation (Equation 4, 5 and 6) [7]. Thus, the combination of Fenton-based processes with photocatalysis is an effective strategy to improve the efficiency of water pollutant removal [8].

$$\text{Photocatalyst} + h\upsilon \rightarrow e^- + h^+ \tag{1}$$

$$e^- + O_2 \rightarrow O_2^{\bullet-} \tag{2}$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \tag{3}$$

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^\bullet \tag{4}$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HOO^\bullet + H^+ \tag{5}$$

$$Fe^{3+} + H_2O + h\upsilon \rightarrow Fe^{2+} + H^+ + HO^\bullet \tag{6}$$

The aim of our work is to understand the simultaneous coupling of photocatalytic and Fenton-based processes that are triggered using a nanostructured material. To this end, we report the use of TiO_2 nanotube layer that are modified at its surface by Fe(III) (Fe-TNT) as an efficient dual-function nanomaterial for efficient degradation of caffeine in water. The study of Fe-TNT layers provides new insight into the coupling mechanism of photocatalysis and Fenton-based processes as an innovative water treatment technology.

2. Materials and Methods

TNT layers were prepared by electrochemical anodization at 60 V for 4 h of 1.5 cm x 1.5 cm Ti foil (99.7%, Sigma Aldrich) in an electrolyte composed of ethylene glycol (EG, CentralChem) and ammonium fluoride (NH_4F, CentralChem). The as-deposited TNT layers were then annealed at 450 °C in the air for 2 h. Fe surface-modified TNT layers were prepared by spin-coating technique of $Fe(NO_3)_3$. $9H_2O$ solution of different concentrations (10 µM, 100µM, 1mM, 10mM, 100mM) in IPA, followed by annealing at 450°C in the air for 2 h to obtain Fe(III) surface-modified TNT (Fe-TNT). The morphology of Fe-TNT was analyzed by SEM/EDX (Tescan Lyra III). The crystalline phase composition was determined by XRD (PANalytical X-ray; Cu K_α, $\lambda = 1.5418$ Å).

The photo-induced degradation of caffeine solution (CAF, ReagentPlus®, Sigma Aldrich; 20 ppm) using Fe-TNT with different concentration of Fe was studied under solar-like light (HQI TS–OSRAM 400 W, 1.3 mW cm^{-2} in the range 335 – 380 nm). The photocatalysis and Fenton-based processes were performed with and without 1mM H_2O_2, respectively. All the photo-induced experiments were performed at pH = 3 in 30 mL solution with constant air bubbling for 4 h. Before irradiation, the mixtures were placed in the dark for 30 min to reach adsorption/desorption equilibrium. To investigate the degradation extents of CAF, 0.5 mL of the mixture was sampled out every 30 minutes and quenched into 100 µL MeOH. The absorbance of caffeine and its degradation byproducts was followed at 272 nm by a UV-vis spectrophotometer (Jasco V-530). In addition, the stability of the Fe-TNT nanomaterials was investigated by determining the amount of Fe leached in the solution during CAF degradation. To this end, 0.5 mL is sampled out every 30 min and mixed with 60 µL of 0.5M ascorbic acid (to reduce aqueous Fe(III) into Fe(II)), 50 µL of 20 mM ferrozine solution (to form Fe(II)-ferrozine complex), and 100 µL of phosphate buffer solution. The complex absorbance along with its extinction coefficient (27900 cm^{-1} M^{-1} at 562 nm) were used to estimate the concentration of leached iron by the Beer-Lamber equation.

3. Results and Discussion

The XRD patterns of TNT and the different Fe-TNT (**Figure. 1**) confirm the presence of the TiO_2 anatase phase (ICDD 03-065-5714). The diffractions of metallic Ti (ICCD 00-044-1294) are from the foil which supports the nanotube layers [9]. From the XRD patterns, the presence of iron oxide or oxohydroxide cannot be detected by XRD for two reasons: (i) the annealing temperature is not high enough to get crystalline compound, and (ii) the amount of deposited Fe(III) is low. It worth noting that higher annealing temperature than 450 °C was not used to avoid conversion of anatase into rutile TiO_2 phase. To confirm the presence of iron on the surface of TNT, EDX analyses are performed (**Table. 1**) and the iron ratio is estimated in the range 0.1 – 1.5 at%. Such analysis also supports XRD measurements since the atomic ratio Ti:O is approximatively 1:2 (**Table. 1**). The morphology of TNT and Fe-TNT is investigated by SEM (**Figure. 2**). The images reveal the nanotubular structure of Fe-TNT with an average diameter of the nanotube of about 120 nm.

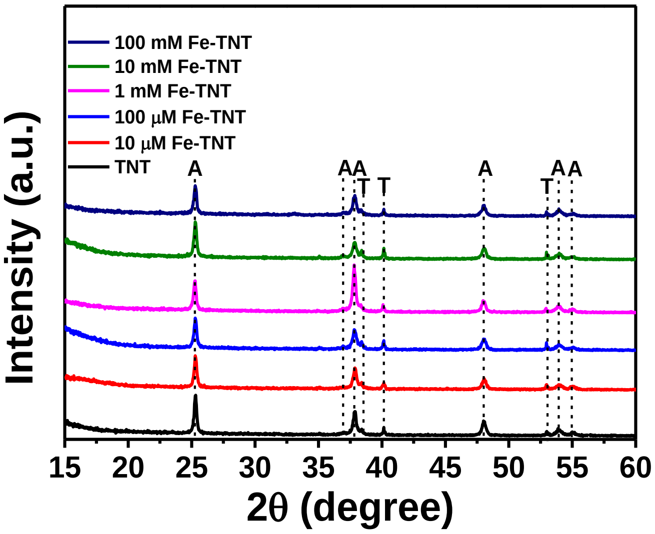

Figure 1. XRD patterns of TNT and Fe-TNT after annealing at 450 °C

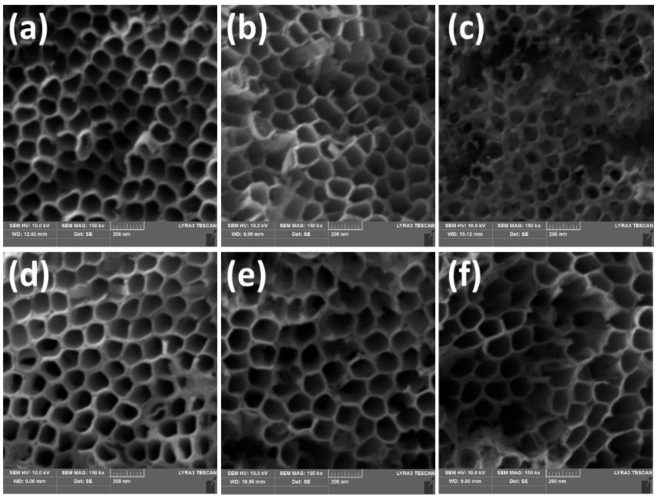

Figure 2. SEM images of TNT and Fe-TNT - (a) TNT, (b) 10μM Fe-TNT, (c) 100μM Fe-TNT, (d) 1mM Fe-TNT, (e) 10mM Fe-TNT, (f) 100mM Fe-TNT

Table 1. EDX analysis of Fe-TNT. *(ND: Non detectable)*

TNT Modified Fe	Carbon (at%)	Oxygen (at%)	Iron (at%)	Titanium (at%)
10μM Fe-TNT	2.24	65.47	ND	32.29
100μM Fe-TNT	1.88	62.96	0.12	35.05
1mM Fe-TNT	1.93	60.29	0.39	37.37
10mM Fe-TNT	2.45	60.25	0.43	36.87
100mM Fe-TNT	4.82	57.32	1.56	31.87

The degradation extents of CAF after 4 h reactions with Fe-TNT under solar-like radiation with and without H_2O_2 are presented in Table. 2. In the absence of H_2O_2, the degradation of CAF increases from 22% to 30% and 25% using 10μM Fe-TNT and 100 μM Fe-TNT, respectively, compared to non-modified TNT. At higher Fe(III) concentration, the degradation efficiency of CAF strongly decreases to 0%. This observation is explained by the increase of •OH production (data not shown) probably due to a positive effect of Fe(III) on the separation of e^-/h^+ pair. In addition, photo-Fenton reaction (*Equation*6) might occur since small amount of iron is leached into the solution. However, as the concentration of Fe(III) increases at the surface of TNT, the photocatalytic process is limited. It can be a consequence of iron aggregates that deactivate photocatalytic TiO_2 sites. On the other hand, in the presence of H_2O_2, the degradation of CAF increases from 27% to 100% for TNT modified by Fe(III) in the range 10 μM – 100 mM, respectively. The observed increase is due to a strong contribution of Fenton-based processes (Equations 4-6) along with H_2O_2 photolysis (Table. 2). The contribution of generation of •OH by reaction of H_2O_2 with photogeneratd e^- might be lower since the photocatalysis decreases with increasing Fe(III) contents in the absence of H_2O_2), However, for non-modified TNT, this latter process is significant with an increase of degradation extent from 22% to 41% without and with H_2O_2, respectively (Table. 2).

Table 2. Degradation extents of CAF after 4 h under solar-like radiation by TNT and Fe-TNT at pH = 3 with and without 1 mM H_2O_2.

TNT Modified Fe	Photocatalysis + H_2O_2	Photocatalysis
TNT	41%	22%
10μM Fe-TNT	27%	30%
100μM Fe-TNT	36%	25%
1mM Fe-TNT	48%	8%
10mM Fe-TNT	100%	0%
100mM Fe-TNT	100%	0%
H_2O_2 photolysis	12%	n.a.

The use of Fe-TNT at pH = 3 as both photocatalytic nanomaterial and Fenton nanocatalyst exhibits some limits: the iron leaching (**Table. 3**). However, such an observation is crucial since it confirms that Fenton-reaction probably occurs in the solution (or close to the nanomaterial/solution interface) and not at the surface of Fe-TNT.

Table 3. Fe leaching from Fe-TNT during CAF degradation under solar-like light at pH = 3 with 1 mM H2O2 (similar value are also obtained in the absence of H2O2).

Time	Fe 10μM	Fe 100μM	Fe 1mM	Fe 10mM	Fe 100mM
0	0.18μM	0.44μM	1.8μM	0.5μM	0.3μM
60	0.26μM	0.1μM	1.8μM	4μM	2μM
120	0.25μM	0.21μM	1.0μM	6μM	4μM
180	0.25μM	0.45μM	1.2μM	11μM	6μM

240	0.53μM	0.65μM	1.3μM	15μM	9μM

Although the iron leaching can be seen as a drawback, it can lead to further development of photocatalysts as loading materials for iron to trigger Fenton-based processes. Indeed, at circumneutral pH, iron leaching does not occur (data not shown), but a selective iron leaching can be performed using non-toxic complexing agents in order to design dual function materials (i.e., heterogeneous photocatalysis coupled to homogeneous Fenton-based processes) [10, 11]. To understand the dual function of such Fe-TNT nanomaterials, insights into the contribution of photocatalysis and Fenton-based processes is assessed using the present 1 mM Fe-TNT under solar-like radiation in the presence of H_2O_2 at pH = 3. Indeed, this Fe-TNT is an optimal sample to determine the contribution of each process (due to their relative weak contributions). A tentative assessment of the process contribution (among the 48% degradation extents) is about 16% photocatalysis along with activation of H_2O_2 by photogenerated e^-, 12% H_2O_2 photolysis, and 27% of Fenton-based processes. Therefore, the use of Fe-TNT is a promising nanomaterial that required further development for potential application in water treatments.

4. Conclusion

The Fe(III)-surface modified TiO_2 nanotube layers (Fe-TNT) were successfully prepared using electrochemical anodization technique and spin-coating method. The CAF degradation at pH = 3 under solar-like radiation by Fe-TNT is the most efficient in the presence of H_2O_2 due to a strong contribution of Fenton-based processes. It is worth noting the Fenton-based reactions do not occur at the surface of the materials but in the solution since iron leaching is observed. Although it can be seen as a drawback due to the limited stability of Fe-TNT, it can open new research direction for designing photocatalysts as loading materials for iron to trigger Fenton-based processes. Indeed, at circumneutral pH, a selective iron leaching using non-toxic complexing agents can be performed, so dual function materials are formed (i.e. heterogeneous photocatalysis coupled to homogeneous Fenton-based processes). Therefore, the use of Fe-TNT layers as dual function nanomaterials (i.e. both photocatalytic and Fenton nanocatalyst) is promising for wastewater application.

Author Contributions: Conceptualization: O.M; Methodology: O.M., M.M., G.P.; Investigation: S.G, G.K.T., M.B.H., V.L., T.R., L.S.; Writing-original draft preparation: S.G., O.M.; Writing—review and editing: S.G., O.M.; Supervision: O.M.; Funding acquisition: S.G., O.M.; All authors have read and agreed to the published version of the manuscript.

Acknowledgement: This work was partially supported by the Scientific Grant Agency of the Ministry of Education, Science, Research and Sport of the Slovak republic (VEGA project No. 1/0062/22) and by the project USCCCORD (ZoNFP: NFP313020BUZ3) co-financed by the European Regional Fund within the Operational Programme Integrated Infrastructure.

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