Effect of Doping On The Photocatalytic Activity of TiO_2 Nanowires Prepared By the Hydrothermal Method

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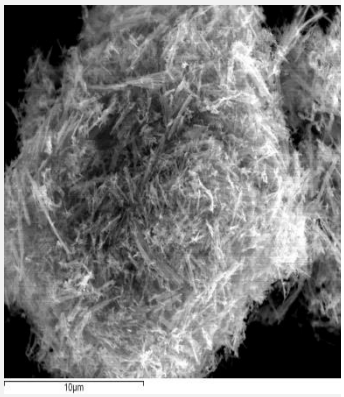
M.O. Honório[1], R. F. P. M. Moreira [1], A. Mendes[2], L. Andrade [2] (1) Universidade Federal de Santa Catarina, Campus Universitário, Trindade, 88040-900, Florianópolis, Brasil (2) Faculdade de Engenharia, Universidade do Porto, Rua Dr. Roberto Frias, 4200-465, Porto, Portugal; [*]micheline@fe.up.pt*



In this study, TiO_2 nanowires were synthesized by hydrothermal route and the photoactivity under UV radiation, morphology and bandgap energy were evaluated. The material morphology was characterized by SEM, the bandgap energy was quantified by analysis of diffuse reflectance and photoactivity under UV light was assessed by degradation of methylene blue in aqueous solution. TiO_2 nanowires were successfully synthesized, revealing an energy bandgap reduction of approximately 5 % by doping with nitrogen. This results in a reduced photoactivity in the UV region, thus suggesting the possibility of using this material under visible light. Tests in this region will be performed.

1.Background

Titanium dioxide (TiO_2) is a semiconductor material widely used [1-5] in several research fields, such as photocatalysis for environmental applications and bacteria photo-inactivation, hydrogen production via photohydrolysis and dye-sensitized solar cells (DSCs).[6, 7] This versatility of applications is explained by its interesting properties of non-toxicity, excellent energy conversion efficiency, good chemical stability and it is readily available and relatively cheap. Furthermore, TiO_2 shows band edges well positioned, exhibiting strong oxidizing power at ambient temperature and pressure (3.0 V) and the photogenerated electrons are able to reduce oxygen to superoxide (-0.2 V).

Recent studies have suggested that TiO_2 nanowires can provide enhanced charge transport along longitudinal dimension and reduced electron-hole recombination rate. [4, 6, 7] Moreover, doping TiO_2 with nitrogen favours the narrowing of the TiO_2 bandgap, enabling absorption within visible light spectrum.

Bare TiO_2 nanowires can be prepared by hydrothermal method using TiO_2 P25 as precursor, [8] and doped afterwards with non-metals. In this paper, we have synthesized N-doped TiO_2 nanowires by hydrothermal method. The effect of doping in the photocatalytic activity under UV light was studied.

2.Experimental section

Preparation of N-doped TiO_2 nanowires

N-doped TiO_2 samples were synthesized by hydrothermal method. The precursor solution was prepared by adding 1.0 g of TiO_2 (P25 from Evonik, Germany) to 100 mL of a 10 M sodium hydroxide (NaOH) aqueous solution, 2 mL and 4 mL triethilamine (TEA) and stirring for 1 h. The solution was then transferred into a Teflon-line stainless-steel autoclave and treated at 180 ºC for a specific time (72 h and 96 h experiments were performed). After reaction, the autoclave was cooled to room temperature. The doped TiO_2 powder was obtained after filtrating and washing with distilled water and hydrochloric acid (HCl, pH 2) several times until pH 7 is achieved; then the powder was dried at 60 ºC for 24 h. The resultant material was calcined at 700 ºC (at a heating rate of 2 ºC/min). Two different amounts of TEA were considered and the correspondent samples were named according its TEA composition and time of reaction: NF-N(2)-72 and NF-(2)-96 (nanowires sample treated during 72 h or 96 h, respectively, with 2 vol. % TEA) and NF-N(4)-72 and NF-N(4)-96 (nanowires sample treated during 72 h or 96 h, respectively, with 4 vol. % TEA). The undoped TiO_2 was prepared by the same approach and named NF-72 and NF-96 (nanowires treated during 72 h or 96h, respectively). Commercial TiO_2 P25 was used as a reference without further treatment.

Characterization

The examination of morphology of the as prepared samples was performed using a Scanning Electronic Microscope (SEM), JEOL JSM 6301F/Oxford INCA Energy 350. Diffuse reflectance was measured in the range of 240-800

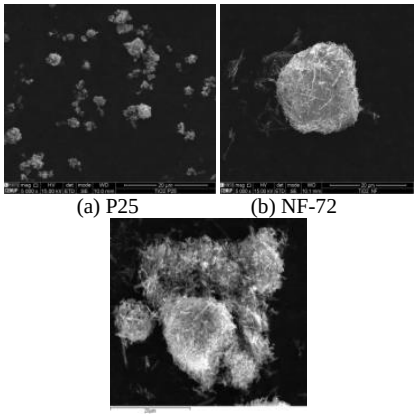
nm using a spectrophotometer UV 3600 (Shimadzu) for determining the bandgap energy (E_g). Thermogravimetric analysis (TG 209 FI (Netzch) Iris®) was performed from 30 ºC until 990 ºC at a heating rate of 2 ºC/min, in a nitrogen flow of 30 mL/min.

Photocatalytic activity

The photocatalytic activity of the different samples was estimated from the degradation of methylene blue (MB) in a home-made apparatus with UV lamp as radiation source (irradiance at the surface of the mixture of 10 W/m^2). For the photocatalytic experiments, 50 mg of photocatalyst was suspended in 100 mL methylene blue (MB) solution with concentration of 10 mg/L in a beaker. The suspension was magnetically stirred for 30 min without light exposure. Then, the photocatalytic reaction was started by turning on the UV light. After, sample was collected, centrifuged. Then, the absorbance was determined at 665 nm.

3. Results and Discussion

The nanowires structures were characterized by SEM. Figures 1 and 2 show the morphologies of nanowires synthesized after 72 h and 96 h, with and without addition of TEA. Independently of the operating parameters (time of synthesis and percentage of TEA) it is observed that all the samples exhibited the presence of nanowires and the formation of agglomerates. In particular, there is a tendency to have an increased size of the agglomerates when time of synthesis is higher and when 4 % of TEA is added to the sample; this may occur since these operating conditions conduct to the production of longer nanowires.

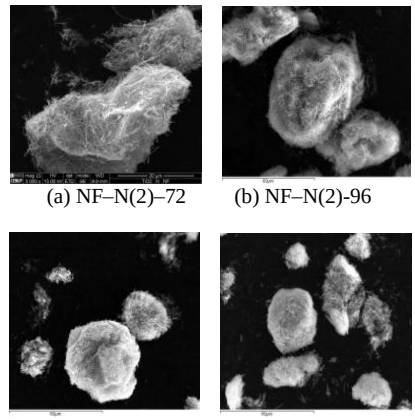


(a) P25 (b) NF-72

(c) NF-96

Figure 1. SEM images of TiO_2 material synthesized without TEA at different times of synthesis: a) P25; b) reaction time of 72 h; and c) reaction time of 96 h.

Thermogravimetric analysis (TGA) - Figure 3a – of the synthesized nanowires during 72 h and with 4 vol.% of TEA presented the highest mass loss, whereas nanowires synthesized during 96 h presented the lowest – Figure 3b.



(a) NF–N(2)–72 (b) NF–N(2)-96

(c) NF–N(4)- 72 (d) NF–N(4)-96

Figure 2. SEM images of TiO_2 nanowires synthesized with different % TEA and different synthesis times: a) 2 vol.% of TEA and reaction time of 72 h; b) 2 vol.% of TEA and reaction time of 96 h; c) 4 vol.% of TEA and reaction time of 72 h; d) 4 vol.% of TEA and reaction time of 96 h.

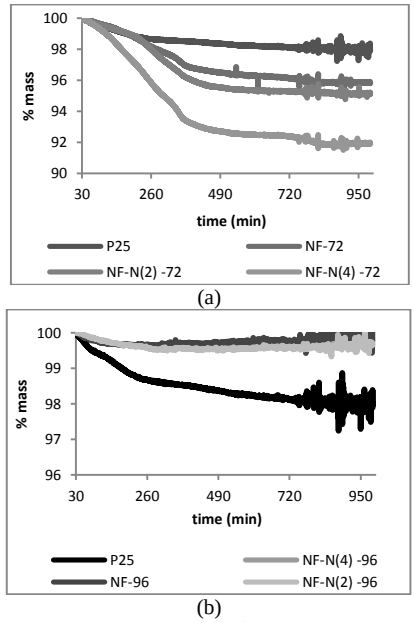


Figure 3. TGA comparison of nanowires synthesized with P25 (Evorik) and different TEA percentages with: a) reaction time of 72 h; b) reaction time of 96 h.

The determination of the bandgap E_g was estimated from the diffuse reflectance (R) in the range of 240 – 800 nm and by applying the

Kubelka-Munk function (KM = F(*R*)), plotting $(KMxh\nu)^{½}$ versus energy (eV) The results are shown on Figure 4.

No difference in the bandgap energy of the photocatalysts with different doping levels was observed. Though, the 72 h nanowires, which showed the shortest length, presented an approximately 5 % reduced bandgap when compared with P25.

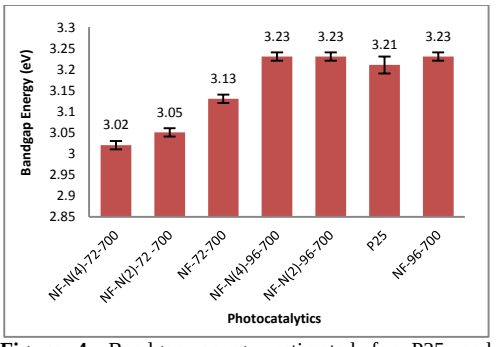


Figure 4. Bandgap energy estimated for P25 and nanowires synthesized.

Photocatalytic activity

Methylene blue dye was used as organic pollutant to evaluate the photocatalytic activity of doped TiO_2 nanowires. In Figure 5 it is shown the UV light photocatalytic activity for the degradation of MB for TiO_2 photocatalysts synthesized with different doping amounts of TEA and during different synthesis times. The undoped and doped nanowires samples with 96 h of reaction time showed efficiency for MB degradation similar to P25 under UV light (≈ 90 %). Regarding the nanowires samples prepared with 72 h of reaction time (NF-72, NF-N(2)-72 and NF-N(4)-72), they presented low photocatalytic degradation efficiencies, around 50 %, and since the bandgap was slightly decreased, this may indicate that these nanowires can have potential in the photodegradation of pollutants under visible light. This will be confirmed with visible tests photodegradation that are ongoing.

4.Conclusion

In this work TiO_2 nanowires were synthesized by the hydrothermal method using P25 as precursor. Different preparation times and different amounts of TEA (confirmed by SEM images) were used. The energy bandgap of the nanowires was estimated based on the diffuse reflectance; bandgaps between 3.02 and 3.13 eV were obtained for 72 h reaction time. The lowest value of bandgap was obtained for 4 vol.% of TEA. This bandgap reduction was indeed reflected in lower values of efficiency of the MB degradation under UV light (Figure 5). Visible light experiments are ongoing.

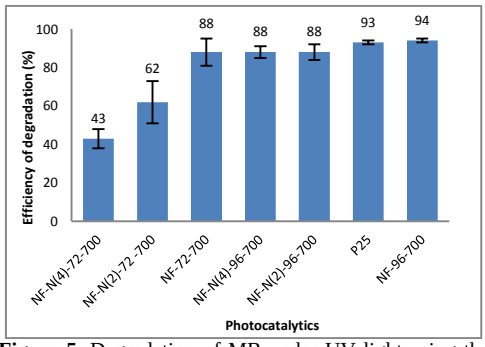


Figure 5. Degradation of MB under UV light using the TiO_2 material synthesized, with and without TEA for different synthesis times, measured by the reduction of absorbance in 665 nm after 4 hour, compared with P25.

Acknowledgements

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