Strontium-Modified Titanate Nanowires for the Photocatalytic Oxidative Removal of Emergent Pollutants from Water

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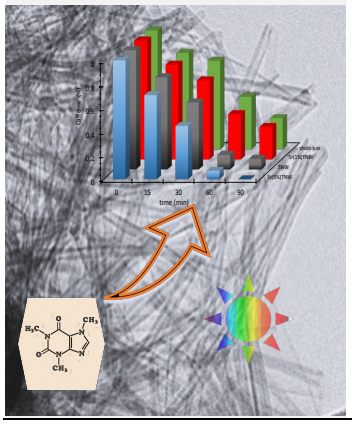

Titanate elongated nanomaterials have been studied as promising catalysts for photoassisted oxidation processes, including emergent pollutants removal. In this work, the synthesis and photocatalytic evaluation of novel strontium-modified titanate nanowires (TNW) is described. Pristine and modified SrTNW were obtained through hydrothermal treatment. Characterization data from XRD, Raman, XPS, TEM, and DRS/PL, indicates no changes in the titanate crystalline structure but agrees with the existence of Sr in 2 distinct positions. The photocatalytic degradation of caffeine, used here as model pollutant, was evaluated under UV–vis and vis radiation. A clear improvement on TNW photocatalytic performance was observed after Sr incorporation. Hybrid films of *g*-C_3N_4 and SrTNW were also evalauted, confirming advantages on photocatalytic activity and stability/reusability.

Introduction

Climate change and environmental degradation are two dramatic issues that threaten the sustainability of humanity. Several ambitious actions and strategies have been proposed worldwide to preserve biodiversity in lakes, rivers, and wetlands and to reduce particularly harmful pollution from microplastics and pharmaceuticals. Within this framework, it is essential the development of environmentally friendly technologies and solutions for the removal of contaminants from aquatic systems.

Photocatalysis, using semiconductor nanomaterials as catalysts, has been seen as a promising AOT to degrade organic pollutants, including *Pharmaceutic and Personal Care Products*. TiO_2 nanoparticles (NPs) have been thoroughly investigated as photocatalyst, but their high charge recombination rate and wide bandgap are drawbacks for its practical application, especially under sun irradiation. Titanate nanotubular materials have been attracted increasing attention in recent years as an alternative to TiO_2, since they have similar structure and bandgap, but larger surface area and ion exchange ability [1]. In addition, tailor the photocatalytic properties of these materials can be easily attained by both improving the absorption of visible light and/or reducing the recombination of photogenerated charge carriers. Doping TNW with transition metals has been recognised as an effective strategy for achieving such goal. [2]

Here, TNW modified by Sr doping (1% and 5%), were synthesized. After, distinct amounts of Sr(%)TNW and *g*-C_3N_4 particles were immobilized on an surface using a layer-by-layer method to produce hybrid films. Both, SrTNW NPs and hybrid films were successfully studied for the degradation of caffeine.

Material and Methods

Sr-TNW (1%, 5%), were synthesized using a hydrothermal approach. [1,2] Hybrid films containing both (Sr)TNW and *g*-C_3N_4 were obtained using experimental procedure shown in Figure 1.

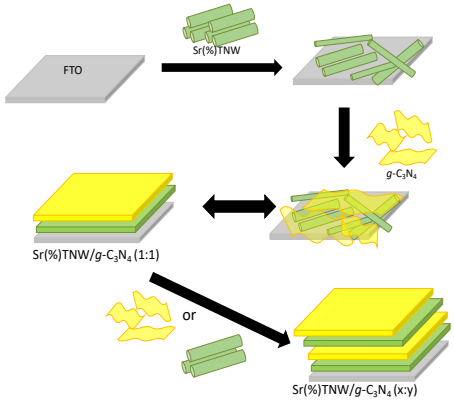

Figure 1. Scheme for hybrid films preparation

Photocatalytic ability of SrTNW NPs and SrTNW/*g*-C_3N_4 hybrid films was studied for degradation of an emergent pollutant model, caffeine.

Results and Discussion

Despite the similarities between the XRD patterns of Sr doped and pristine TNW powders (Figure 2), an increase in the peak's intensity with the increase of dopant concentration is visible for all samples. This effect has been reported for nanocrystalline Sr-TiO_2 particles and supported on a random substitution of larger Sr^{2+} in the TiO_2 lattice; thus, causing structural strain and disorder in the crystalline structure.[3]

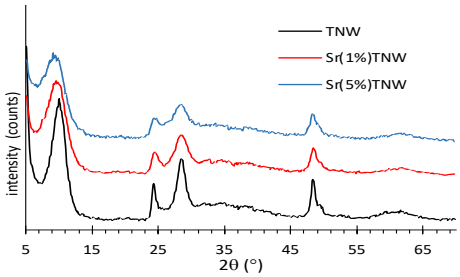

Figure 2. XRD patterns of pristine TNW, Sr(1%)TNW, and Sr(5%)TNW samples.

The morphology of the prepared samples was analysed by TEM. Elongated nanoparticles, typical of titanates, were observed in all the samples. Figure 3 shows a TEM image of Sr(1%)TNW sample. To further investigate the Sr impact in TNW samples, they were analysed by Raman spectroscopy. Some changes in the spectra of Sr modified TNW powders were observed. Through DRS analysis, no substantial changes on the optical behaviour of TNW were observed due to Sr incorporation.

Photocatalytic activity of the Sr-doped TNW NPs was evaluated using caffeine as model pollutant. The best photo-catalytic performance was attained by the Sr(5%)TNW powder, with the complete degradation of caffeine after 90 min of irradiation.

Anticipating the recycling possibility of such materials and to improve photocatalytic performance and stability, exfoliated *g*-C_3N_4 was combined with Sr(5%)TNW to produce hybrid films.

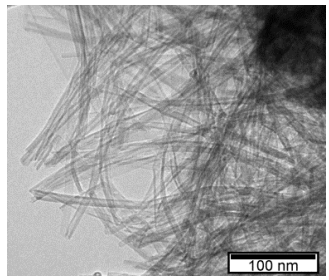

Figure 3. TEM image of the Sr(1%)TNW sample.

The best removal results (Figure 4), under visible radiation, were obtained using the 2:1 Sr(5%)TNW:*g*-C_3N_4 hybrid film.

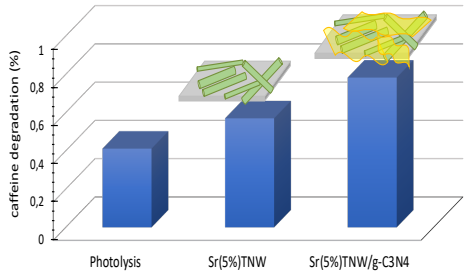

Figure 4. Degradation profiles of a caffeine solution (20 mg L^{-1}) using distinct photocatalysts and visible radiation.

The use of *g*-C_3N_4 contributes for the improvement of the nanocomposite film stability, allowing its reuse during, at least, four consecutive runs without losing its photocatalytic performance.

Conclusions

In this work, crystalline TNW modified with Sr, Sr(1%)TNW and Sr(5%)TNW, were successfully produced. Characterization data indicate that Sr can be effectively incorporated into TNW crystalline structure, with the metal being in 2 distinct positions. An enhancement of the photocatalytic performance for caffeine removal was attained with the Sr-doped TNW samples; being the Sr(5%)TNW the best photocatalyst. Additional improvements on the Sr-TNW films photocatalytic activity were attained by combine it with layered *g*-C_3N_4.

Acknowledgments

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