Enhancing Photocatalytic and Bactericidal Activity Post-Illumination of WO_3/TiO_2 Heterojunction

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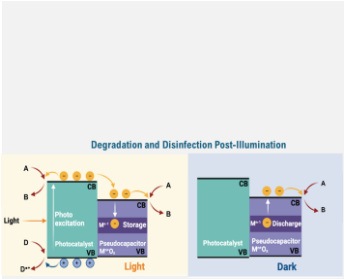

The light intermittence in photocatalytic processes implies instabilities and losses. Persistent photocatalysis materials circumvent this issues and present photocatalytic activity post-illumination. This work presents the development of a material composite that have catalytic activity after being exposed to UV light, like a photocatalytic memory, this type of material is composed of a pseudocapacitor and a photocatalyst. In this case, the heterojunction proposed is WO_3/TiO_2, being the titanium oxide the photocatalyst, and the tungsten oxide is responsible for the storage of electrons. Herein are presented the synthesis methodologies, including photocatalytic tests simulating intermittent light and bactericidal tests. This type of material comes to aggregate and enhance the photocatalysis area, providing smooth operation overcoming instabilities caused by sharp light intermittency periods in the system.

Introduction

A process that uses photocatalysts has a weakness in its sensitivity to the amount of sunlight that reaches a given area. The presence of clouds and their movement can cause unpredictable and sharp losses in solar radiation, leading to instabilities during operation. To address the issue of natural intermittent radiation for on-site applications, a novel approach is to use persistent photocatalysts [1]. Developing these sorts of catalysts consists of combining photocatalysts with charge storage materials, so part of the charge generated by the photocatalyst during irradiation is followed by a discharge during periods of no light. A pseudocapacitor can work as a storage material and supply this demand. Thus, they allow a full-time generation of free radicals. This project aims to elaborate metal oxide heterojunctions consisting of a photocatalyst (TiO_2) and a pseudocapacitor (WO_3). It is based on developing and studying a synthesis route for persistent photoactive nanoparticles by microwave-assisted solvothermal and hydrothermal methods, a fast synthesis method. Furthermore, the materials were subjected to photocatalytic tests simulating intermittent light and bactericidal tests.

Material and Methods

The metal oxides were synthesized using microwave-assisted methods [2]. The photocatalytic tests consisted of dye degradation using UV light. Three types of photocatalysis occurred: traditional photocatalysis, realistic photocatalysis (intermittent light simulation), and persistent photocatalysis (the material was previously charged, and then the catalytic reaction took place in the dark). The Live/Dead Cells staining method evaluated the bactericidal action using the PI and SYTO9 dyes analyzed under a fluorescence microscope (Olympus IX71).

Results and Discussion

The SEM images (Fig. 1 A, B and C) show that tungsten oxide has agglomerate sizes ranging from 500 nm to 5 um, and titanium dioxide has particle sizes between 3 and 5 um. The heterojunction shows that TiO_2 has some WO_3 particles deposited on the surface. Fig. 1D shows an XRD comparison of the heterojunction and the oxides separately. XRD analysis indicated the hexagonal and anatase phases for WO_3 and TiO_2.

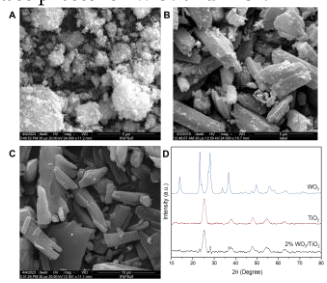

Figure 1. SEM images **A** WO_3, **B** WO_3/TiO_2 and **C** TiO_2 and **D** XRD results for all samples.

The diffractogram of the heterojunction shows a mixture of the peaks of the oxides already analyzed. It clearly shows that the peaks referring to titania are more intense, indicating a higher concentration in the mix, and some slight peaks refer to the 2% of WO_3 in the system. The heterojunction's XPS spectra, Fig. 2, evidenced the presence of suboxides/defects. In the W4f spectrum, the peaks refer to the +5 and +6 states, 33.8 and 36 eV and 34.4 and 37 eV, respectively. The Ti2p spectra show Ti^{+4}, Ti^{+3}, and Ti^{+2}, and at the O1s level, a peak at approximately 528.8 eV related to the Ti-O bond and a peak at 529.3 eV related to the W-O.

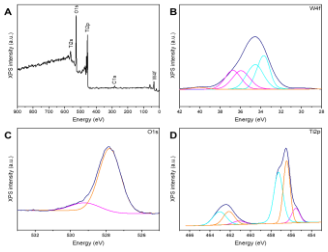

Figure 2. **A** XPS spectrum **B** W4f level, **C** O1s level and **D** Ti2p level.

Fig. 3A shows the results of traditional photocatalysis during the degradation of Congo Red 20 ppm, using UVC light. Both systems showed moderate dye degradation, but the most interesting is shown in Fig. 3B. It shows a realistic photocatalysis test, starting with 30 minutes of adsorption, with no adsorption during this time. This is followed by 30 minutes with UV light, where the dye degradation begins, and the reaction continues in total darkness. During this last part, the systems continued to degrade the dye, i.e., they showed photocatalytic activity after illumination.

Another photocatalytic test was carried out. This time, the catalysts were charged for 2 hours, received UV light, and then added to the dye solution in the dark. Again, after receiving light, the catalysts continued the reaction. This same test was carried out for comparison purposes with commercial TiO_2P25, which showed no degradation.

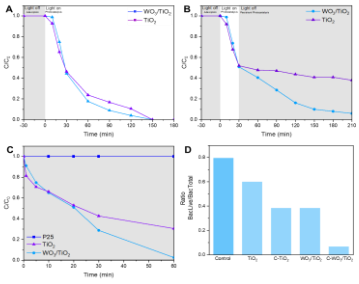

Figure 3. Congo Red degradation **A** Traditional, **B** Realistic and **C** Persistent Photocatalysis and **D** Bactericidal test reduction.

In addition to the photocatalytic tests, bactericidal tests were carried out against *E. Coli*. The catalysts were tested before and after charging by UV light, i.e., the bacteria remained in the dark the whole time. According to the results shown in Fig. 4, the charged catalysts showed bactericidal activity, and the heterojunction system is outstanding, with a 91% reduction compared to the control data.

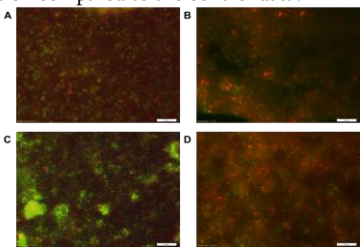

Figure 4. Microscope images from Live/Dead Cells staining method. A TiO_2, B TiO_2 "charged", C WO_3/TiO_2 and D WO_3/TiO_2 "charged".

Conclusions

The metal oxides chosen as photocatalysts and pseudocapacitors performed well in each function. The defects present in the structures of each oxide were essential for the operation of continuous photocatalysis. Materials with persistent photocatalysis properties can be widely applied, and the possibility of having a material working full-time is critical to avoid production losses. Besides the application in processes that require the degradation of organic pollutants or disinfection, a system that can provide high charge storage density and high catalytic performance can also be applied in energy conversion. This type of material can still be further explored and evolved to ensure more operating time and a more controlled release of the stored energy.

Acknowledgments

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