CRYSTALLINE AND AMORPHOUS SEMICONDUCTOR OXIDE: ITS PHOTOCATALYTIC ACTIVITY

Morales Sánchez M.A., Valencia de Lima J.I., Luna Flores A., Agustín-Serrano R.,
Cervantes Tavera A.M., Hernández Santiago A.A.
Benemérita Universidad Autónoma de Puebla

Abstract. In this work the photocatalytic activity of an amorphous material (aTiO2), a semicrystalline material (scSnO2) with its respective crystalline phases (cTiO2 and cSnO2) is compared. For the evaluation of the photocatalytic activity, a solution of Rhodamine B was used. In both cases, the corresponding crystalline phase has less photocatalytic activity in Rhodamine B degradation. The aTiO2 is 50% more effective than the cTiO2 and the 40% more scSnO2 than cSnO2.

Keywords: photocatalysis, amorphous, semi-crystalline

Introduction.

In recent years, photocatalysis has attracted the attention of researchers because of its wide application, not only in the treatment of wastewater and air decontamination, but also in obtaining sustainable energy. Among the most used materials is TiO_2 due to its low cost properties, low toxicity, chemical and physical stability and high efficiency in the degradation of organic compounds [1,2]. However, TiO_2 has the disadvantage (like many other semiconductor oxides used in photocatalysis) of activating only with ultraviolet light due to its bandgap (3.2 eV). For a long time it has been believed that semiconductor oxides with higher photocatalytic activity are those that are in well-defined crystalline phase. However, Chen et al. [3] propose that a structural disorder in TiO_2 nanocrystals can improve their photocatalytic activity and even extend their photocatalytic activity using radiation visible. This provides new alternatives for the investigation of photocatalytic activity investigation of the photocatalytic activity of amorphous materials and / or slightly crystalline materials, which, in the case of TiO_2, may be better than the crystalline material in some applications [4-6].

In this work, amorphous, semi-amorphous and crystalline materials (TiO2 and SnO2) are obtained by a simple microwave-assisted methodology in order to compare their photocatalytic activity in the degradation of Rhodamine B, showing that an amorphous or semi-crystalline material may be higher photocatalytic activity than the same material in its crystalline phase.

Experimental part.

Synthesis of $aTiO_2$

The synthesis of $aTiO_2$ is carried out according to the following methodology: in a ball flask 15 mL of 1-decanol are added, heated to 80 ° C for 10 min, then 2 mL of titanium butoxide are added, stirred 10 min and 4 ml deionized water were added while stirring for an additional 7 min. Then a 4-min microwave treatment is given to obtain amorphous TiO_2 ($aTiO_2$). The photocatalyst is rinsed with acetone and methanol and dried at 80 ° C for 30 min.

Synthesis of SnO2

The synthesis of SnO_2 was carried out using as solvent 1-butanol, as precursor $SnCl_2 \cdot 2H_2O$ and adding NH_4OH for its hydrolysis. The reactions were carried out by a microwave treatment for 5 min, thus obtaining amorphous SnO_2 ($aSnO_2$). The $aSnO_2$ is used as raw material to obtain crystalline SnO_2 ($cSnO_2$) by heat treatment at 600 ° C for 2 hrs and to obtain semi-crystalline SnO_2 ($scSnO_2$) by dispersing it in 50 mL of water with microwave treatment for 30 min.

Tests of photocatalytic activity

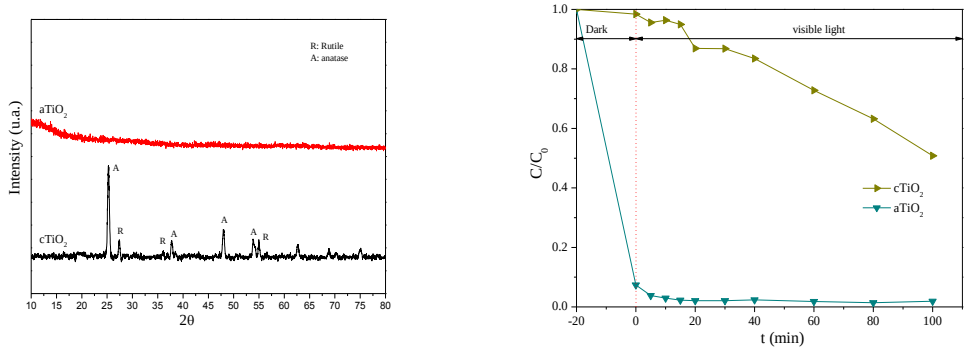
Photocatalytic tests are performed in a system previously described [7]. For each degradation test 15 mg of photocatalyst were dispersed in 60 mL of a solution of Rhodamine B (5 ppm). The process is monitored by UV-vis aliquots at regular intervals of time for 100 min. In both cases it is compared with the corresponding crystalline phase.

Results.

Figure 1a shows the X-ray diffraction patterns (DRX) for the synthesized sample $aTiO_2$ and $cTiO_2$ for comparison purposes. In this figure only the flat baseline for the $aTiO_2$ is appreciated which confirms the amorphous nature of the samples. The diffraction pattern for $cTiO_2$ shows the two phases: anatase and rutile.

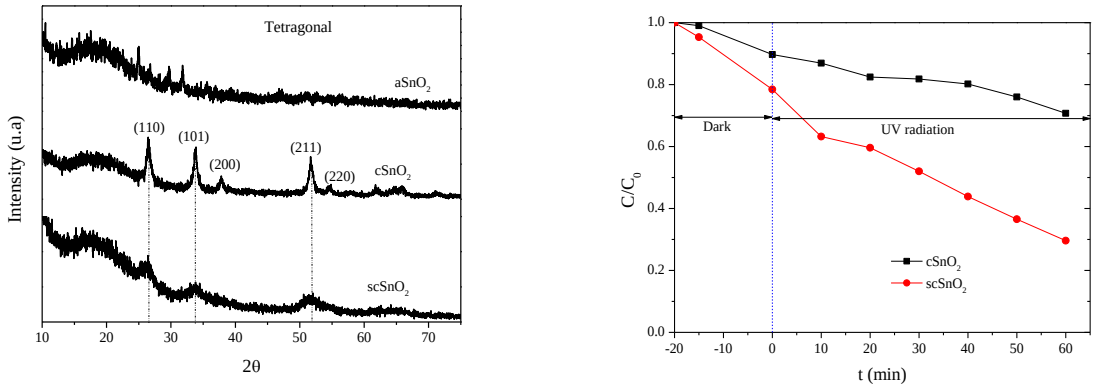
Figure 1b shows the degradation rate of Rhodamine B with respect to the time in which we can observe that when using $aTiO_2$ as the photocatalyst, we obtain about 90% decrease in the concentration of Rhodamine B due to the great absorption capacity of this amorphous photocatalyst, and in 20 min has a little more than 99.5% of degradation of Rhodamine B. Not so for $cTiO_2$ that after 100 min of irradiation with visible light only achieves a percentage of degradation of 50%.

The X-ray diffractograms shown in Figure 2a indicate the production of amorphous, semi-amorphous and crystalline SnO_2 in the tetragonal phase. Figure 2b shows the variation of the concentration of Rhodamine B during the photocatalysis process. In this figure it can be seen that the $scSnO_2$ photocatalyst being semi-crystalline has an absorption capacity greater than $cSnO_2$, because it absorbs more Rhodamine B (about 10% more) on its surface. The percent degradation after 60 min irradiation with ultraviolet light is 30% and 70% for $cSnO_2$ and $scSnO_2$, respectively. The $aSnO_2$ did not show photocatalytic activity.



a) b)

Figure 1 – a) DRX for the amorphous TiO_2 ($aTiO_2$) and for the commercial TiO_2 Degussa P25 ($cTiO_2$). b) Degradation of Rhodamine B (5ppm) under the action of $aTiO_2$ and $cTiO_2$ when irradiated with visible light



a) b)

Figure 2 – a) DRX for SnO_2 synthesized samples). b) Degradation of Rhodamine B (5ppm) under the action of $cSnO_2$ and $scSnO_2$ when irradiated with UV light

Conclusion.

By means of a simple microwave-assisted methodology, amorphous ($aTiO_2$, $aSnO_2$), semi-crystalline ($scSnO_2$) and crystalline ($cSnO_2$) materials were synthesized. The evaluation of its photocatalytic activity in the degradation of Rhodamine B shows a dependence on the structural defects of the material, showing a greater photocatalytic activity for $aTiO_2$ and $scSnO_2$, with respect to its crystalline phases $cTiO_2$ and $cSnO_2$, respectively. The analysis of the effect of this structural disorder with respect to the transport of charge, as well as in the process of recombination of electron-hole pairs is proposed as a future work.

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