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RESEARCH ON OBTAINING TIO_2-CNF NANOCOMPOSITES

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Abstract: TiO_2 is one of the most promising catalysts because of its superior photocatalytic performance, easy availability, long-term stability, and nontoxicity. It is well known that the titanium dioxide photocatalysis is widely used in a variety of applications and products from different fields, so for this paper we obtained and investigated TiO_2 nanocomposites doped with carbon nanofibers. For this we used the sol-gel method and different reagents: two titanium precursors (titanium isopropoxide and tetrabutyl orthotitanate), two solvents and two neutralizing agents. The samples were characterized by methods like Scanning Electron Microscopy and Transmission Electron Microscopy. The results were used to determine the most suitable reagents and particle size for obtaining crystalline TiO_2-CNF. It could be noticed that the average size of the particles is 20 nm and that the crystallinity has increased after calcination at 400°C.
Key words: titanium oxide, carbon nanofibers, nanocomposites, doping, crystallinity.

1. INTRODUCTION

TiO_2 appears to be the most promising and suitable material among photocatalysts, because of its superior photocatalytic activity, chemical stability, low cost, and nontoxicity. In addition, it also attracted much attention about the coordination of titanium dioxide with carbon nanomaterials in order to take advantage of outstanding properties of these materials such as high electrical conductivity, nano-sized diameter, high adsorption and absolute black level which create a synergistic effect with titanium dioxide that is leading to the formation of a catalyst system with great photochemical activity on the surface [1]. However, composites have been reported to disperse TiO_2 nanoparticles on substrates, and recently, TiO_2–carbon nanocomposites have been found to be attractive because carbonaceous materials can act as thermally stable and electrically conductive substrates. The photocatalytic properties are of special interest for the neutralization of pollutants and harmful organics. [2]. Therefore, a great number of researches have been done to improve photochemical activity of this catalyst in visible light region. Obtaining TiO_2 nanoparticles using sol-gel method has been performed by some researchers [3-7], others reported modifications of the oxide in order to reduce the energy bandgap and increase the photocatalytic activity under the visible light radiation [8-13]. Because of their ultra-high specific surface area, excellent electrical properties, very high chemical resistance, and acceptable mechanical properties, CNFs are materials of choice for catalytic support. Among the different materials, carbon nanotubes and nanofibers (CNF) have been preferred due to their mechanical and electronic properties. Carbon fibers are high aspect ratio graphitic fibers, and possess great technical and industrial importance due to their wide-ranging properties, like very high strength to weight ratio, superior electrical and thermal conductivity, excellent chemical resistance. Carbon nanostructures also offer new opportunities for photovoltaic conversion and photocatalysis due to increased contact area and good electrical conductivity. Based on valuable developments in the nano-era, wide potential applications for carbon fibers were projected and huge efforts were focused on their synthesis, in order to improve their properties, which caused an exponential increase in the number of related research articles published in the last two decades [14-19]. When combined with graphene, TiO_2 acts as a trap for electrons, which facilitates the interfacial electron transfer. For preparation, it is shown that the final properties of the material depend on the size, morphology and crystalline phase. Therefore, the sol-gel method is the most suitable for preparing TiO_2-CNF, since it has advantages such as homogeneity, control over microstructure, compatibility with a variety of precursors, simplicity of the process, low temperature and costs, and low requirements for the purity of the reagents [20, 21].

For this paper we obtained and investigated TiO_2 nanocomposites doped with carbon nanofibers. For this we used the sol-gel method and different reagents: two titanium precursors (titanium isopropoxide and tetrabutyl orthotitanate), two solvents and two neutralizing agents. The samples were characterized by methods like Scanning Electron Microscopy and Transmission Electron Microscopy.

2. EXPERIMENTAL

2.1 Materials

For the experiment we used two precursors: the (TIP) titanium isopropoxide ($C_{12}H_{28}O_4Ti$) from *PANREAC* and (TNB) tetrabutyl orthotitanate ($C_{16}H_{36}O_4Ti$) from *MERCK*.

The first precursor was in solid state and the second in liquid state. For their treatment we used two solvents: ethanol (C_2H_6O) from *PANREAC* and ethyl acetate ($C_4H_8O_2$) from *PANREAC*. As a hydrolyzing agent we used nitric acid (HNO_3) from *PANREAC* and for neutralization we used two solvents: sodium hydroxide 0,1M (NaOH) (*PANREAC*) and ammonia 0,1M (NH_3) (*PANREAC*).

2.2 Sample and reaction preparation

For the preparation of TiO_2-CNF nanocomposites we first added the solvent to the titanium dioxide and stirred until complete dissolving, then the HNO_3 65%, pH= 1.5, to the dissolved CNF, drop by drop while stirring, thus ensuring that the nanofibers remain embedded within TiO_2.

Stirring is maintained for one hour to ensure maximum contact between the phases. After this time, the base is added until it forms a xerogel, maintaining the pH between 9 and 10.

Table 1. Experimental details

Sample	TIP precursor	TNB precursor	Ethanol 96%	Ethyl acetate 99%	HNO_3 65% pH=1.5	NaOH 0.1 M	NH_3 0.1 M	CNF
Unit	[g]	[ml]	[ml]	[ml]	[ml]	[ml]	[ml]	[g]
1	5.7		10	-	50	75	-	1.5
2	-	6.8	10	-	50	75	-	1.5
3	-	6.8	-	10	50	-	80	1.5

The addition of base allows more control over the reaction speed and stimulates the formation of nanoparticles.

Finally, this suspension is dried in the oven in order to remove the excess liquid. When enough time has passed, usually about 24 hours till complete drying, we proceed to grinding the obtained ceramic powder and its characterization using Transmission Electron Microscopy (TEM), Electron Diffraction (EDX) and Scanning Electron Microscopy (SEM).

After the experiment we obtained the following samples to analyse:

-*Sample 1*: obtained using TIP as a precursor, NaOH 0.1 M as a base and ethanol as a solvent;

-*Sample 2*: obtained using TNB as a precursor, NaOH 0.1 M as a base and ethanol as a solvent;

-*Sample 3*: obtained using TNB as a precursor, NH3 0.1 M as a base and ethyl acetate as a solvent.

The reaction details are summarized in Table 1.

2.3 SEM analysis

The SEM and EDX analysis results are presented below. The images from figure 1 show that in sample 1 we obtained quite compact agglomerated particles and even some CNF can be seen.

In both cases the EDX spectra (figure 3) show peaks of C, Ti, and O, but of Ni and S too (the latter two elements are present from the precursors).

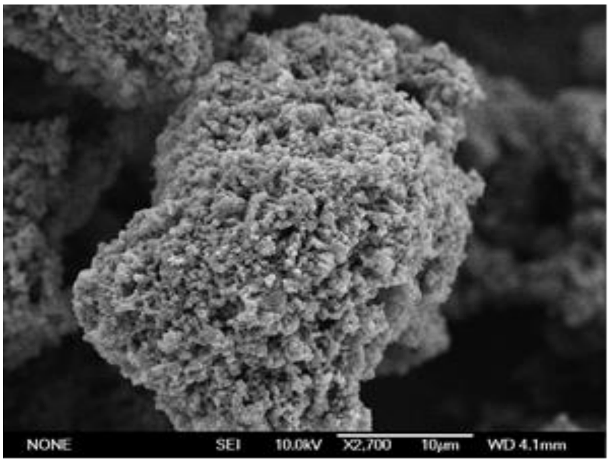
Comparing the two samples, it can be observed that the surfaces of both samples are approximately compact, but we conclude that sample 2 is better than sample 1 due to the increased number of CNF obtained.

The use of NH_3 0.1 M as a base and ethyl acetate as a solvent in sample 3 showed more satisfactory results. The surface is also formed by agglomerated particles, but they are bigger in size and more compact than sample 1 (figure 4).

In the EDX spectrum we can see a new N peak and the same Ti and O peaks corresponding to the TiO_2 matrix. Since this sample gave the best results we proceeded to its calcination and analysed it by TEM.

2.4 TEM analysis

After calcination of sample 3 at 400°C for 2h we performed the TEM analysis. The micrographs indicated that the TiO_2 nanoparticles, which have an average particle size of (10–30)nm, had been successfully grown on the surface of CNF. In figure 5 we can see the CNF as black dots. Also the structure appears more crystalline and we can see the TiO_2 surrounding the CNF.



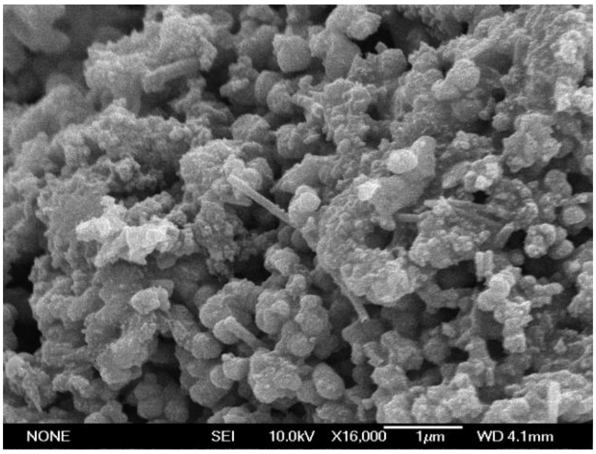


Fig. 1. SEM micrographs of sample 1

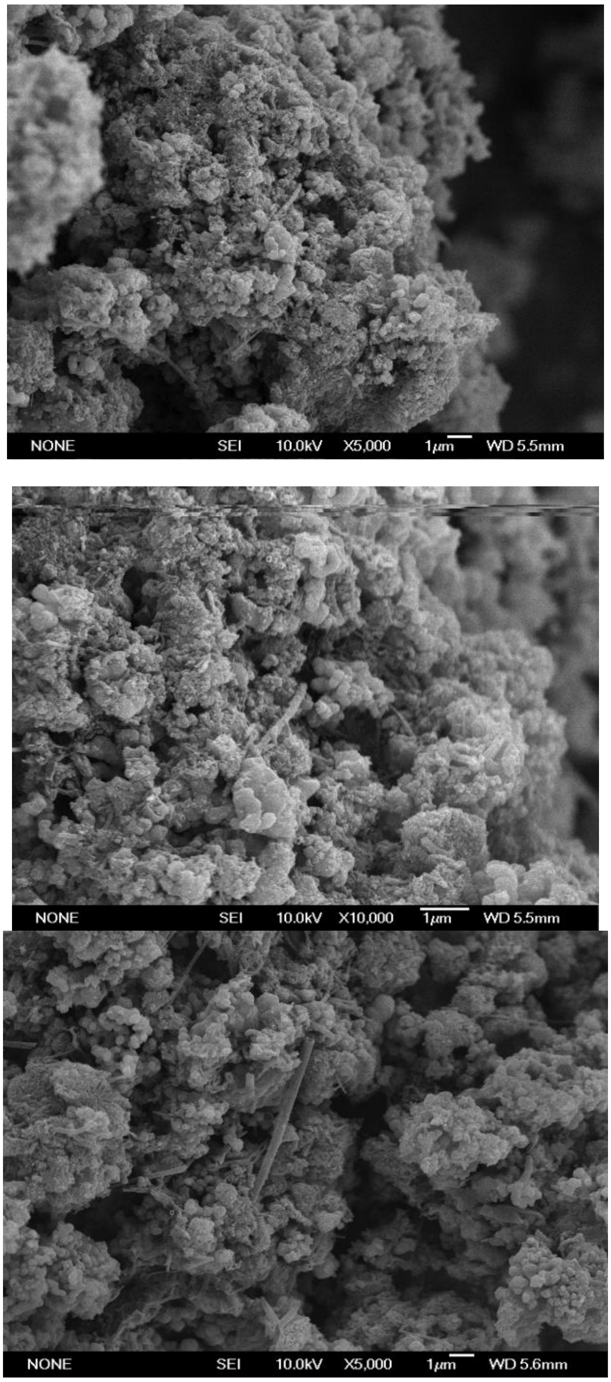


Fig. 2. SEM micrographs of sample 2

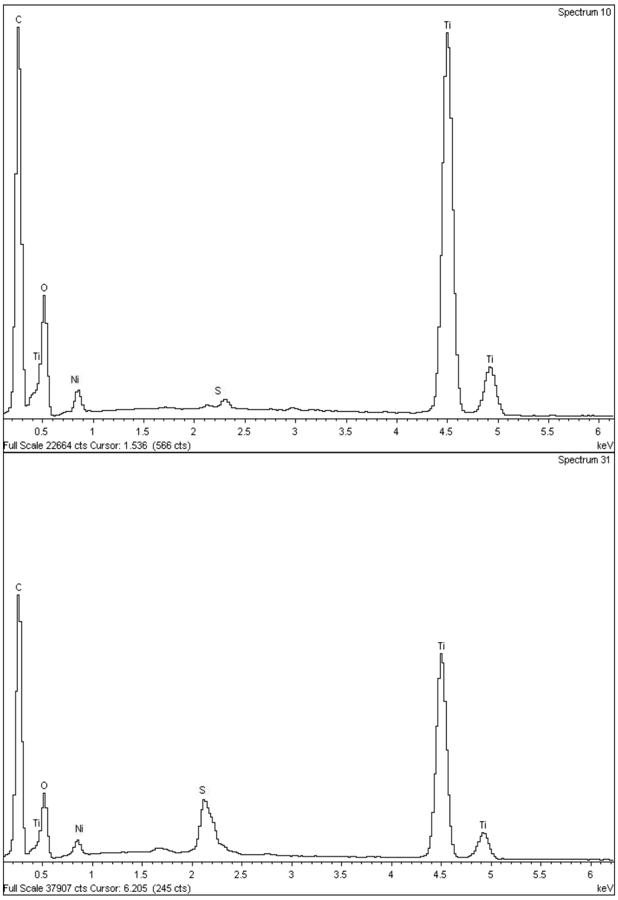
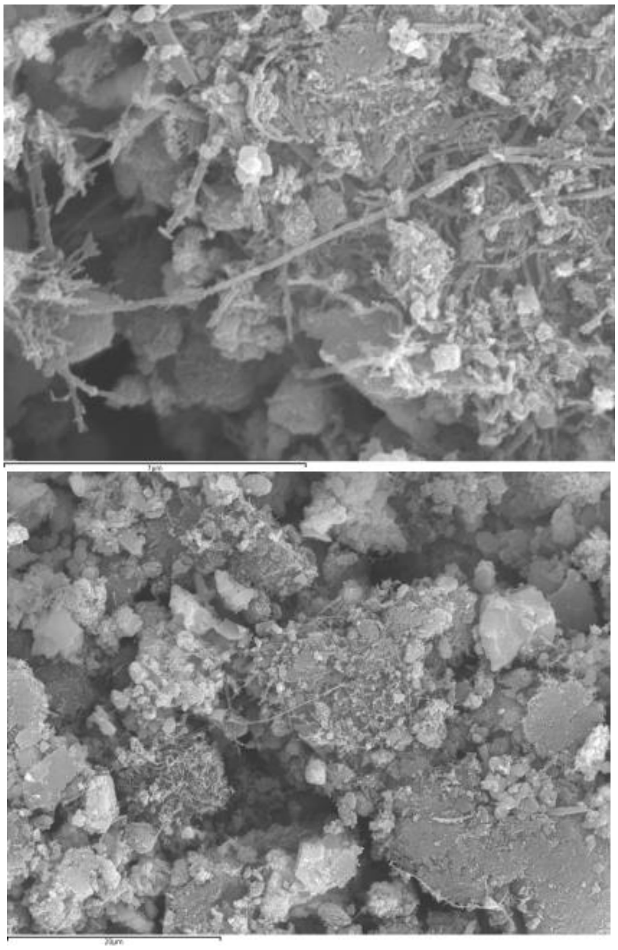


Fig. 3. EDX spectra of sample 1 (up) and sample 2 (down)



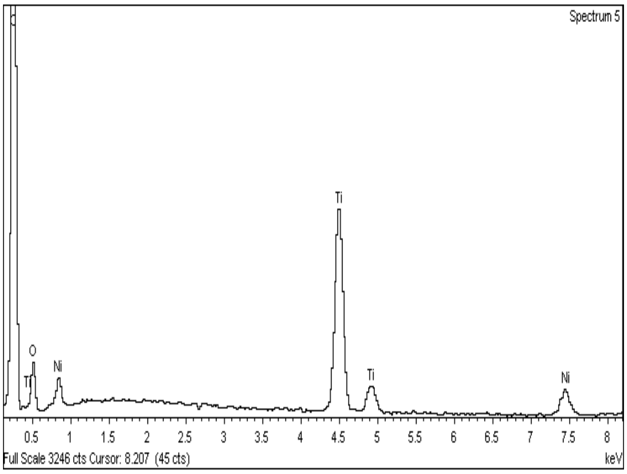
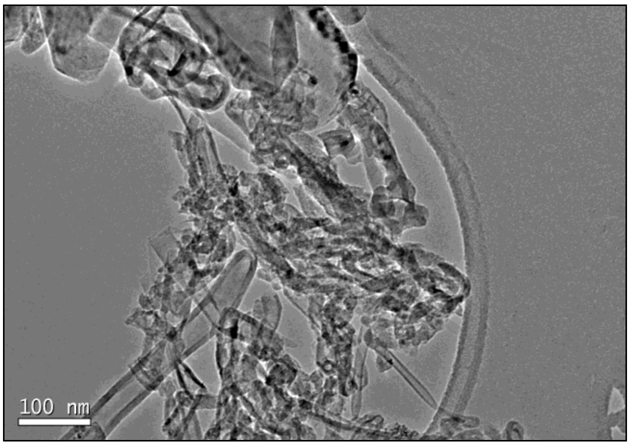
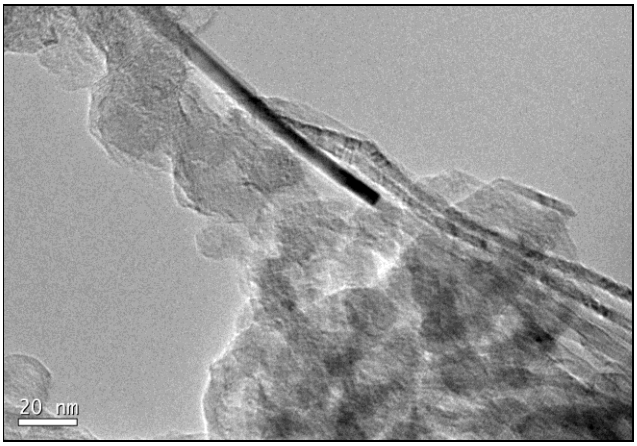
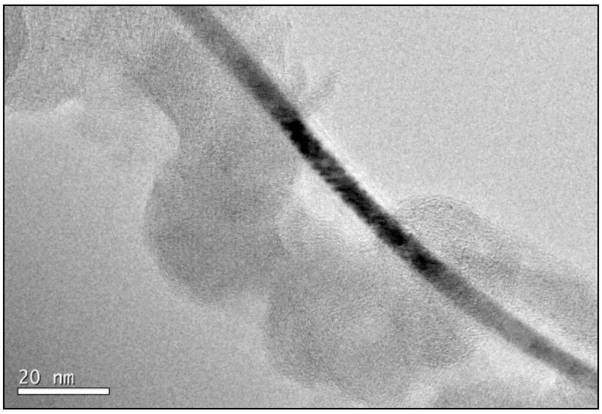
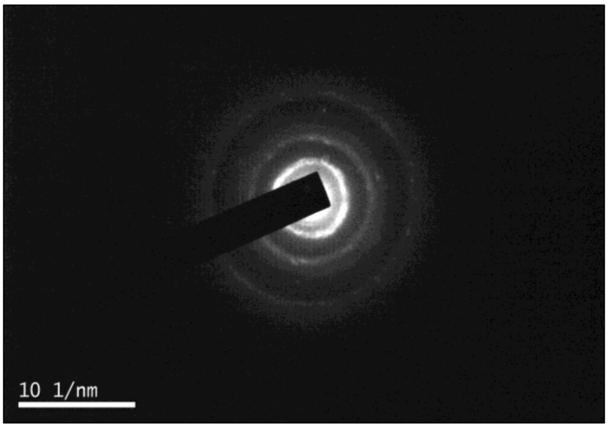


Fig. 4. SEM micrographs and EDX spectrum of sample 3









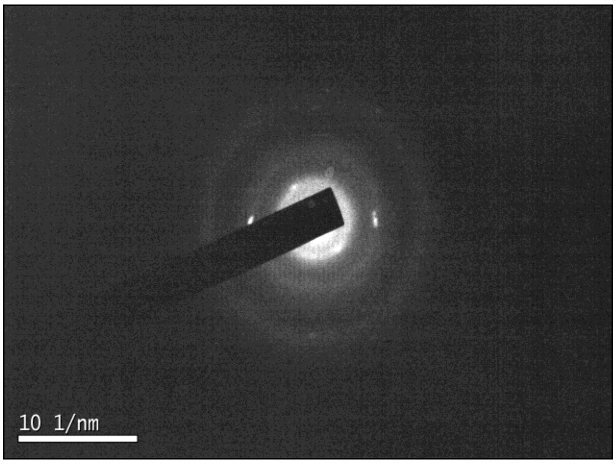


Fig. 5. TEM micrograph and electron diffraction pattern of sample 3

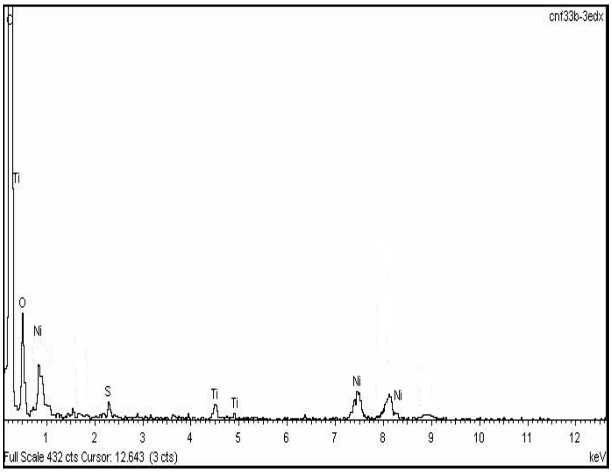


Fig. 6. EDX spectrum of the obtained particles

3. CONCLUSION

The main objective of the paper was to obtain TiO_2-CNF nanocomposites. These nanocomponents were successfully synthesized via sol-gel method with TNB as a precursor, NH_3 M as a base and ethyl acetate as a solvent. The results show that the carbon nanofibers were embedded within two hours by calcination at 400°C. This prevented the agglomeration of TiO2 and significantly increased crystallinity compared to the other samples. Furthermore, using the TEM characterization it was observed that the average particle size was about 20nm. Thus TiO_2-CNF nanocomposites can improve future antibacterial and photocatalytic applications.

4. REFERENCES

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