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Preparation and Performance of TiO_2-ZnO/CNT Hetero-Nanostructures Applied to Photodegradation of Organic Dye

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Water pollution by organic compounds is one of the major challenges faced by industries that use dyeing processes. Thus, some methods were developed for degrading dyes in wastewaters, including heterogeneous photocatalysis by semiconductor oxides. However, these oxides have limited photocatalytic activity due to the fast recombination of photogenerated electron–hole pairs. The aim of this study is the use of a carbon nanotube (CNT) and TiO_2-ZnO oxide junction from modified sol-gel method to promote the degradation of organic dye through the photocatalytic activity of these nanocomposites. TiO_2-ZnO/CNT nanocomposites were studied by X-ray diffraction (XRD), transmission electron microscope (TEM), scanning electron microscope (SEM) and photocatalytic decomposition of organic dyes. The results of photocatalysis show up to 60% the efficiency of the samples in the removal of dye.

Keywords: *TiO_2-ZnO/CNT; nanocomposites; heterogeneous photocatalysis; degradation dye*

1. Introduction

The increasing interest in photocatalysis in recent years is a result of its unquestionable advantages[1]. Photocatalysts have a natural ability to destroy organic pollutants at ambient temperature and can oxidize organic carbon into CO_2 [2].

Oxide semiconductors have been extensively studied and used as photocatalysts to degrade various polluting compounds. Lin and collaborators[3] reported that ZnO is an n-type semiconductor with a wide band gap (3.37 eV). Titanium dioxide or titania (TiO_2) is an n-type semiconductor with a band gap near 3.2 eV[4]. Regarding the photocatalytic activity of TiO_2 and ZnO, this is due to the high number of defects, such as oxygen vacancies, interstitial zinc atoms in donor states, as well as gaps and interstitial oxygen atoms in receivers[5]. Shen and collaborators[6] affirm that the dispersion and surface area, which depend on the method of synthesis, are determining factors in photocatalysis.

Photocatalytic activity is closely connected with the size of nanocrystallites of oxide semiconductors, larger surface areas and higher capacities for adsorbing organics. Lately the use of carbon nanotubes (CNTs) to increase the effectiveness of surface reactions has been more frequently observed[1].

The CNTs associated to oxide semiconductors have been used as chemical sensors, biosensors, nanoelectronics of devices, photovoltaic cells, fuel cells, hydrogen storage, in the treatment of contaminated water and for air heterogeneous photocatalysis, photo reduction of CO_2 and electrodes for solar cells[7]. Nanocomposites can be obtained by several different methods: sol-gel synthesis[8,9], electrospinning[10], electrophoretic deposition[11] and chemical vapor deposition[12], among others. TiO_2 coatings of uniform CNTs were obtained by chemical vapor deposition[13] and by electrospinning[14,15]. Nevertheless, these techniques are not easy and require specialized equipment. However, with the sol-gel method it is possible to obtain a homogeneous and effective coating for photocatalytic performance[16]. The objective this study is to obtain the TiO_2-ZnO/CNT nanocomposite and use it as a catalyst for removal of methyl orange dye in solution.

2. Materials and Methods

In this experimental procedure the following precursors were used: commercial TiO_2 (P25) produced by Degussa and commercial ZnO produced by Sigma-Aldrich; nitric acid p. a. produced by Synth; isopropyl alcohol, deionized water and commercial multi-walled carbon nanotubes (MWCNT) produced by Bayer®. The solutions remained under agitation at 60°C/1h. Subsequently and before completion of the gelation process, the system was filtered at liquid temperature and the retained material was kept at 100°C for 24h. The production of the samples was divided in systems containing: sample obtained MWCNT, commercial TiO_2 and ZnO named NPZ; MWCNT and commercial TiO_2 named NP; MWCNT with commercial zinc oxide named NZ. The samples were characterized by SEM and XRD to investigate the morphologies and crystal structures. Morphology observations were accomplished on JEM 1200EXII-120kV instrument under 12-15 kV acceleration voltage. An X-ray diffractometer PHILIPS diffractometer (Model X'Pert MPD) equipped with a graphite monochromator and a copper anode,

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operating at 40 kV and 40 mA were used in structural analyses performed in a 2θ range of 15°- 80°, with steps of 0.05° for 2s, with Cu Kα radiation. Measures of photocatalytic activity at room temperature were carried in a system of twelve 8 W UV lamps emitting 365 nm of wave length. The dye concentration was set to 1.0×10^{-5} mol/L, while 0.5g nanocomposite was added to 125 ml solution (deionized water and dye) under basic pH. The photocatalytic activity of the composites was evaluated following the decomposition of methyl orange dye under UV light. Initially, the MWCNTs/TiO_2 composites were added to dye solution and kept in the dark for 1h to adsorption. Subsequently, the solution was dispersed using ultrasound for 10 min., after this period the solution was irradiated with UV light. The reaction recipient consisted of a quartz Dreschel bottle fitted with a silicone septum to facilitate withdrawal of samples from the reaction dispersion and the UV lamps are positioned vertically around bottle. Samples were collected periodically from the reactor every 10 min during the 80 min time interval with a syringe and then filtered (pore diameter 0,2 μm) to a 4 mL PMMA cuvette. The absorbance at the wavelength of 465 nm was recorded (Bioespectro SP 200) used to determine the dye concentration of each collected sample. The efficiency of the photocatalytic activity regarding UV-exposure time was determined by measuring transmittance and calculated by comparing the dye concentration (C) in the system with an initial dye concentration (C_0).

3. Results and Discussion

3.1 Microstructure analysis

Figure 1 shows the XRD patterns of TiO_2-ZnO/MWCNT, TiO_2/MWCNT, ZnO-MWCNT, MWCNT, commercial TiO_2. Peaks in the pattern at 26° and 43.4°, relative to planes (002) and (101), respectively, are characteristic of CNTs[17]. These peaks may be apparent on the XRD pattern of the MWCNT sample. The main peak of the anatase phase is 25.4°, concerning plane (101). This plane is very close to the peak on the CNT, and could explain the overlapping of peaks of CNT in the samples containing TiO_2 (NP and NPZn samples) in this position, obstructing the visualization of the carbon peak at 26° in relation to plane (002). In addition, the disappearance of the characteristic peak of the second pattern at 43.4° NTCPMs may suggest homogeneous coating on TiO_2 nanotubes and less aggregated pores in the composite catalysts[2,18].

Figure 2 shows the effect of SEM on the samples. It can be seen that TiO_2 and ZnO is coating the surface of MWCNTs (Figure 2). Although the oxide coatings modified CNT surface, there is irregular distribution of oxides on the bundles of nanotubes and formation of clusters, for there is no homogeneous distribution during the synthesis.

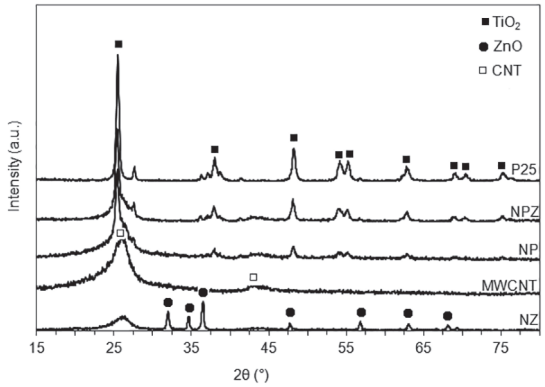

Figure 1: XRD of nanocomposites, multi-walled carbon nanotubes and commercial oxide TiO_2.

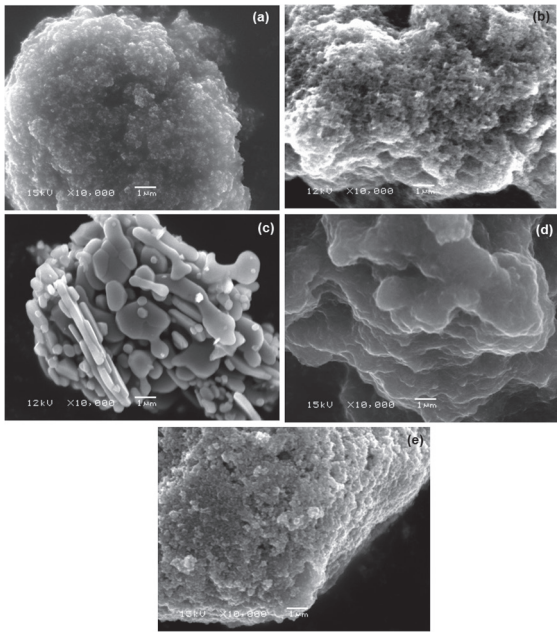

Figure 2: Scanning electron microscope (SEM) images of (a) commercial TiO_2 (P25), (b) TiO_2/MWCNT, (c) commercial ZnO and (d) ZnO/MWCNT and (e) TiO_2-ZnO/MWCNT nanocomposite.

The agglomeration of TiO_2 particles and the CNT-oxides junction can be observed in the morphology of the sample obtained with transmission electron microscopy (Figure 3). The crystallographic planes of TiO_2 can be observed ensuring the presence of the crystalline phase of TiO_2 from P25.

3.2 Photocatalytic Activity

Photocatalytic properties of the samples were analyzed from methyl orange dye decomposition. Figure 4 shows the dependence of C/C_0 versus time t, where C is the concentration of methyl orange dye at a certain time and C_0 is the initial concentration of dye after the adsorption effect in dark during 1h. TiO_2–ZnO/MWCNT was found

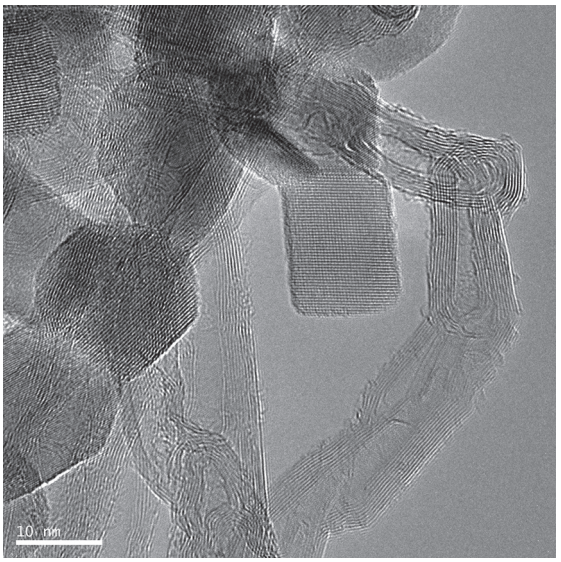

Figure 3: TEM images of the TiO_2/MWCNT nanocomposite (NP sample) at 2.500.000x magnification.

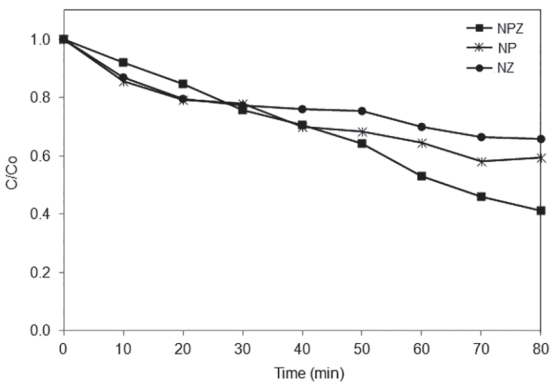

Figure 4: Activity photocatalytic of the nanocomposites on the decrease of the methyl orange dye concentration in solution.

to exhibit higher efficiency and better enhancement in UV light decomposition, compared to other samples.

According to Czecha and collaborators, there are two reasons for the increased activity of NPZ nanocomposites on other samples: (I) e^- formed due to excitation migrate to the nanotubes, (II) CNTs affect inhibition of e−/h+ recombination in ZnO-TiO_2. Another factor that stimulated the increase in dye removal compared to NP and NZ can be a greater number of active sites. In view of the aforementioned aspects, it can be affirmed that there are more hydroxyl radicals, formed during the reaction in aqueous solution, in the TiO_2/MWCNT system than in TiO_2 [1]. In the case of the tested nanocomposites, the role played by MWCNT in the nanocomposite would not be exactly increase the adsorbing capacities, but inhibiting e^-/h^+ recombination and augment the number of formed *OH radicals. Thus, in the tested nanocomposites, MWCNT is a photo sensitizer[19].

4. Conclusions

TiO_2-ZnO/MWCNT was synthesized by an easy-to-use modified sol-gel method from commercial precursors for photoactivity tests of these materials that were assessed through the degradation of methyl orange dye in an aqueous solution under UV irradiation. The photocatalytic effect on TiO_2-ZnO/MWCNT nanocomposites occurs not only because of the adsorption of CNTs, but also because of electron transfer between CNTs and oxides, which removes the dye from the solution. The NPZ sample (TiO_2-ZnO/MWCNT) showed satisfactory photocatalytic activity results, which can be compared to ZnO/MWCNT and TiO_2/MWCNT samples, although other factors are involved in the photocatalytic activity, such as the conditions of synthesis, TiO_2 particle size, the nature of CNTs, pore distribution and the composition of phases. The addition of TiO_2 and ZnO on MWCNT to promote dye decomposition increases the photocatalytic activity. Morphology can be associated with the homogeneity demonstrated by TiO_2-ZnO-MWCNT nanocomposites. Therefore, all the samples showed evidence of coating formation. Transmission electron microscopy images indicated that TiO_2 nanocomposites reached a similar average particle size of approximately 20 nm (the diameter of MWCNTs), while the nanotubes have an average diameter of approximately 10nm.

5. Acknowledgements

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6. References

1. Czecha B, Budab W, Pasieczna-Patkowska S, Oleszczuk P. MWCNT–TiO_2–SiO_2 nanocomposites possessing the photocatalytic activity in UVA and UVC. *Applied Catalysis B: Environmental*. 2015;162:564-572.

2. Shaari N, Tan SH, Mohamed AR. Synthesis and characterization of CNT/Ce-TiO 2nanocomposite for phenol degradation. *Journal of Rare Earths*. 2012;30(7):651-658.

3. Lin CS, Hwang CC, Lee WH, Tong WY. Preparation of zinc oxide (ZnO) powders with different types of morphology by a combustion synthesis method. *Materials Science and Engineering: B*. 2007;140(1-2):31-37.

4. Jarzebski ZM, Marton JP. Physical Properties of SnO_2 Materials: I. Preparation and Defect Structure. *Journal of The Electrochemical Society*. 1976;123(7):199C-205C.

5. Ullah R, Dutta J. Photocatalytic activities of ZnO nanoparticles synthesized by wet chemical techniques. In: *2006 International Conference on Emerging Technologies*; 2006 Nov 13-14; Peshawar, Pakistan. p. 353-357.

6. Shen W, Li Z, Wang H, Liu Y, Guo Q, Zhang Y. Photocatalytic degradation for methylene blue using zinc oxide prepared by codeposition and sol–gel methods. *Journal of Hazardous Materials*. 2008;152(1):172-175.

7. Leghrib R, Felten A, Pireaux JJ, Llobet E. Gas sensors based on doped-CNT/SnO_2 composites for NO_2 detection at room temperature. *Thin Solid Films*. 2011;520(3):966-970.

8. Zhang K, Zhang FJ, Chen ML, Oh WC. Comparison of catalytic activities for photocatalytic and sonocatalytic degradation of methylene blue in present of anatase TiO_2-CNT catalysts. *Ultrasonics Sonochemistry*. 2011;18(3):765-772.

9. Bouazza N, Ouzzine M, Lillo-Ródenas MA, Eder D, Linares-Solano A. TiO_2 nanotubes and CNT–TiO_2 hybrid materials for the photocatalytic oxidation of propene at low concentration. *Applied Catalysis B: Environmental*. 2009;92(3-4):377-383.

10. Aryal S, Kim CK, Kim KW, Khil MS, Kim HY. Multi-walled carbon nanotubes/TiO_2 composite nanofiber by electrospinning. *Materials Science and Engineering: C*. 2008;28(1):75-79.

11. Cho J, Schaab S, Roether JA, Boccaccini AR. Nanostructured carbon nanotube/TiO_2 composite coatings using electrophoretic deposition (EPD). *Journal of Nanoparticle Research*. 2008;10(1):99-105.

12. Yu H, Quan X, Chen S, Zhao H. TiO_2–Multiwalled Carbon Nanotube Heterojunction Arrays and Their Charge Separation Capability. *Journal of Physical Chemistry C*. 2007;111(35):12987-12991.

13. Ma L, Chen A, Zhang Z, Lu J, He H, Li C. In-situ fabrication of CNT/TiO_2 interpenetrating network film on nickel substrate by chemical vapour deposition and application in photoassisted water electrolysis. *Catalysis Communications*. 2012;21:27-31.

14. Moya A, Cherevan A, Marchesan S, Gebhardt P, Prato M, Eder D, et al. Oxygen vacancies and interfaces enhancing photocatalytic hydrogen production in mesoporous CNT/TiO_2 hybrids. *Applied Catalysis B: Environmental*. 2015;179:574-582.

15. Frontera P, Malara A, Stelitano S, Fazio E, Neri F, Scarpino L, et al. A new approach to the synthesis of titania nano-powders enriched with very high contents of carbon nanotubes by electro-spinning. *Materials Chemistry and Physics*. 2015;153:338-345.

16. Jitianu A, Cacciaguerra T, Benoit R, Delpeux S, Béguin F, Bonnamy S. Synthesis and characterization of carbon nanotubes–TiO_2 nanocomposites. *Carbon*. 2004;42(5-6):1147-1151.

17. Yu Y, Yu JC, Yu JG, Kwok YC, Che YK, Zhao JC, et al. Enhancement of photocatalytic activity of mesoporous TiO2 by using carbon nanotubes. Applied Catalysis A: General. 2005;289(2):186-196.

18. Gao B, Chen GZ, Puma GL. Carbon nanotubes/titanium dioxide (CNTs/TiO_2) nanocomposites prepared by conventional and novel surfactant wrapping sol–gel methods exhibiting enhanced photocatalytic activity. *Applied Catalysis B: Environmental*. 2009;89(3-4):503-509.

19. Cendrowski K, Jedrzejczak M, Peruzynska M, Dybus A, Drozdzik M, Mijowska E. Preliminary study towards photoactivity enhancement using a biocompatible titanium dioxide/carbon nanotubes composite. *Journal of Alloys and Compounds*. 2014;605:173-178.