

Structure of Ni nanoparticles/TiO₂ films prepared by sol-gel dip-coating

A. García-Murillo^{*}, E. Ramírez-Meneses^{*}, J. Ramírez-Salgado^{**},
G. Sandoval-Robles^{***}, V. Montiel-Palma^{****}, H. Dorantes-Rosales^{*****},
P. Del Angel-Vicente^{**}

^{*} Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada-IPN
Unidad Altamira, Km. 14.5 Carretera Tampico-Puerto Industrial, C.P. 89600,
Altamira, Tamaulipas. México., angarciam@ipn.mx, esramirez@ipn.mx

^{**} Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo, Eje Lázaro Cárdenas No. 152,
C.P. 07730, México, D.F., ramirezj@imp.mx, pangel@imp.mx

^{***} Tecnológico de Cd. Madero Instituto Tecnológico de Ciudad Madero
Av. 1° de Mayo esq. Sor Juana Inés de la Cruz s/n Col. Los Mangos C.P.89440
Cd. Madero Tamaulipas, México., jgsandor@hotmail.com

^{****} Centro de Investigaciones Químicas, Universidad Autónoma del Estado de Morelos,
Av. Universidad 1001, Colonia Chamilpa C.P. 62201 Cuernavaca, Morelos, México.,
vmontielp@ciq.uaem.mx

^{*****} Departamento de Metalurgia, ESIQIE - IPN, C.P. 07300 México, D.F., hdorantes@ipn.mx

ABSTRACT

Titania thin films were synthesized by sol-gel dip-coating method with metallic Ni nanoparticles (~10 nm) from an organometallic precursor. Titania matrix and Ni nanoparticles were prepared separately. The precursors employed to prepare Titania were titanium isopropoxide, isopropanol, methanol and acetic acid. Nickel nanostructures were synthesized from Ni(COD)₂ (COD=cycloocta-1,5-diene) under H₂ atmosphere in THF with 1,3-diaminopropane as stabilizer.

Colloidal solution of Ni nanoparticles was added to sol. Ni/TiO₂ sol system was used to coat glass spheres substrates and further heat treatment at 400 °C.

The photocatalytic activity of the Ni/TiO₂ films was evaluated in H₂ evolution from decomposition of ethanol using a mercury lamp for UV light irradiation. The prepared Ni/TiO₂ was characterized using AFM, UV-Vis, TEM and HR-TEM.

Keywords: sol-gel, thin films, nickel, nanoparticles, organometallic.

1 INTRODUCTION

Metallic nanoparticles as catalyst have been extensively studied due to their particular properties which are quite different from those of bulk materials, for example their large surface area.

Titanium oxide has a great importance due to its excellent photocatalytic properties[1] as well as their industrial applications related to photo-splitting of water[2]

photocatalyst[3], photovoltaic devices[4]. However, TiO₂ exhibits a relative high energy bandgap (~ 3.2 eV) and can only be excited efficiently by high energy UV irradiation that constrains the practical usage of the TiO₂. Efforts have been made to extend the energy absorption range of TiO₂ from UV to visible light or to further improve the photocatalytic activity of TiO₂ by adding foreign metallic elements[5,6]. Ag can serve as electron trap aiding electron-hole separation, and can also facilitate electron excitation by creating a local electric field. Nanocrystalline TiO₂/Ag composite thin films were evaluated by degrading methylene blue UV exhibiting good photocatalytic efficiency[7]. Another element of interest to improve photocatalytic performances is nickel, titania thin film with metallic Ni nanoparticles on its surfaces showed high efficiency in photocatalysis of hydrogen evolution from decomposition of ethanol[8].

On the other hand, On the other hand, the synthesis of metal nanoparticles has received considerable attention due to their unusual properties and potential applications. A number of methods such as hydrazine reduction of nickel chloride[9], electrochemical[10], thermal evaporation [11], laser-assisted gas phase photonucleation [12], hydrogen plasma metal reaction[13], physical vacuum deposition (PVD) process[14] and organometallic method[15] have been employed to obtain nickel nanoparticles. Additionally, many researchers have reported various synthetic methods for nickel nanoparticles supported on the surfaces of others materials.

Nickel nanoparticles with a diameter of 1-10 nm can be supported on the surface of titania particles[16,17]. A large variety of methods have been developed to prepare TiO₂

films by sol-gel process in which dip-coating[18], chemical vapor reductive deposition (CVRD)[8], MOCVD[19], aerosol-assisted process[20], etc. Comparing to these methods the sol-gel process possesses many merits. Metallic particles could be included homogeneously into the sol allowing coating onto various materials even pure metals.

Therefore, in this paper we investigated the feasibility of preparing Ni nanoparticles/TiO₂ thin films grown onto commercial glass spheres by sol-gel dip-coating technique. The as-deposited Ni/TiO₂ films were characterized by TEM, HR-TEM, XRD and AFM. The photocatalytic properties were evaluated by degrading ethanol under UV-irradiation.

Additionally, we report that Nickel nanoparticles deposited onto the surface of the glass spheres improve the separation of photo-produce electron-hole pairs, resultantly enhance the photocatalytic activity of TiO₂[21].

2 EXPERIMENTAL

2.1 Synthesis of metallic nanoparticles

The reaction was carried out, as a standard procedure in a Fischer-Porter bottle. In a typical procedure, a solution of THF (50 ml) including 500 mg of the precursor Ni(COD)₂ (Aldrich) and 1,3-diaminopropane (99%, Aldrich) 5 equivalents per Ni atom was reacted at 70 °C for 20 h, under dihydrogen pressure (3 bar), in Fischer-Porter bottle leads to the formation to dark gray colloids. The reaction is slow at lower temperatures[15]. The obtained solutions were purified by hexane washings. Finally, the resulting solution was evaporated in vacuum until the residue was completely dry.

2.2 Synthesis of of titanium oxide “sol” with Ni nanoparticles

Figure 1 shows the schematic flowchart of the experimental procedure. Titanium tetraisopropoxide (Ti(OiPr)₄ (99.9 %, Aldrich) was mixed with isopropanol (iPrOH-Fermont) and stabilized in presence of acetic acid acetic (AcOH-Fermont), with a molar ratio AcOH/Ti=5.84. The obtained solution was diluted with methanol. The solution was then stirred at room temperature for 1 h. After the reaction time a stable yellowish “sol” is obtained. Then, the metallic nanoparticles were dispersed into the titanium “sol” forming a gray colloidal stable solution.

2.3 Elaboration of Ni/TiO₂ thin films by “dip-coating” technique

Commercial glass spheres used as substrates (3 different diameter sizes: 6 mm, 4 mm and 3 mm) were carefully cleaned with methanol and were wet uniformly with the

Ni/TiO₂ sol using a withdrawal speed of 2.5 cm min⁻¹. After film deposition stage the sample was heat-treated in an oven at 100 °C for 15 min with the aim of remove the most volatile organic compounds and a second coating was done. Finally, the sample was thermally treated at 400 °C for 3 h in order to densify and promote the crystallization of the film.

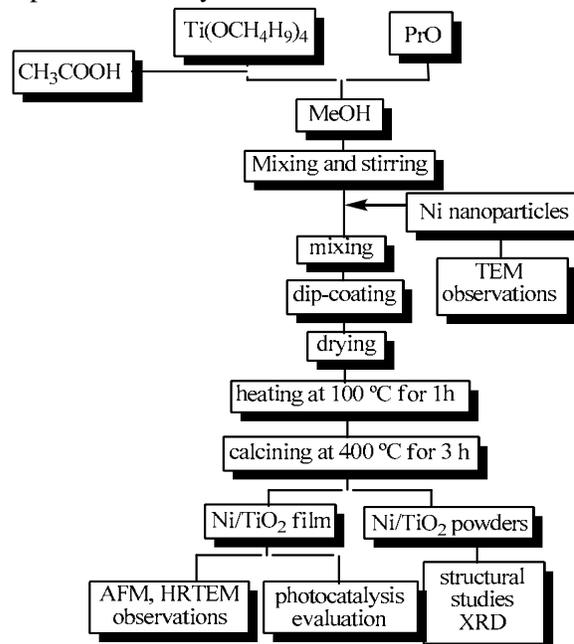


Figure 1. Flowchart of the experimental procedures

3 RESULTS AND DISCUSSIONS

3.1 Phase composition

The phase of the sample was determined by XRD (D8 Advance Bruker, Germany) using a Cu K α radiation. Figure 2 shows the XRD patterns of heat-treated TiO₂ and Ni/TiO₂ films. It can be found that the TiO₂ film pattern (a) and Ni/TiO₂ film (b), exhibited nanocrystalline anatase-TiO₂ phase. It is also notice that not additional XRD peaks corresponding to Ni addition can be revealed. This may be attributed to the well dispersed nanocrystalline Ni particles in the TiO₂ matrix, which are not large enough for XRD detection. The XRD also revealed the absence of any other characteristic peaks of a mixed oxide phase being formed due to an interaction between Ni and TiO₂ support.

3.2 AFM studies

Atomic force microscopy AFM observations of TiO₂ and Ni/TiO₂ films were carried out at room temperature using a Nanoscope IV (Veeco D3100). Figure 3 (a-b) shows the AFM top-view image of TiO₂ and Ni/TiO₂ films respectively. Figure 3(a) shows AFM image corresponding to TiO₂ film heat treated at 400 °C for 3 h which is

characterized for mean roughness (Ra) of 1.747 nm and a RMS (Rq) of 2.219 nm. The TiO₂ nanosized grains formed on the glass surface was found to be 18.1 nm.

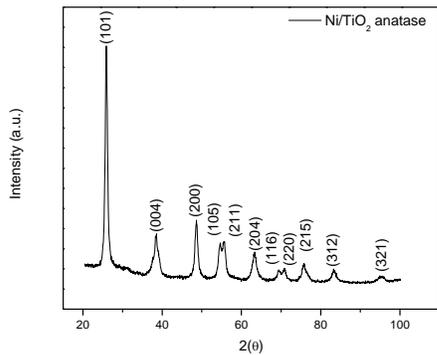
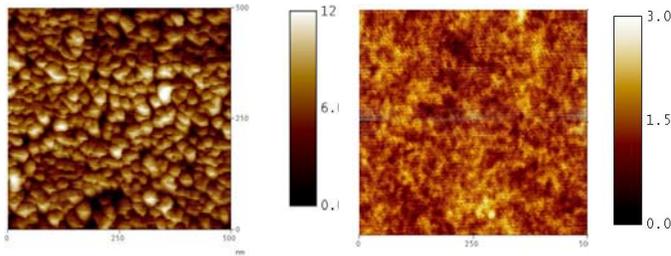


Figure 2. XRD powder patterns of the TiO₂ (a) and Ni/TiO₂ films (b).

Compared to Ni nanoparticles obtained on TiO₂ (Figure 3b) have very fine size with good uniformity in structure and composition. The mean roughness (Ra) was 0.347 nm and the RMS (Rq) was 0.440 nm. The average grain size of Ni/TiO₂ has a diameter of 5 nm (Figure 3b).



(a) TiO₂

(b) Ni/TiO₂



(c) phase imaging of Ni/TiO₂

Figure 3. a) top-view of AFM topography micrographs of TiO₂, b) AFM topography micrographs of Ni/TiO₂, and c) AFM phase imaging of Ni/TiO₂.

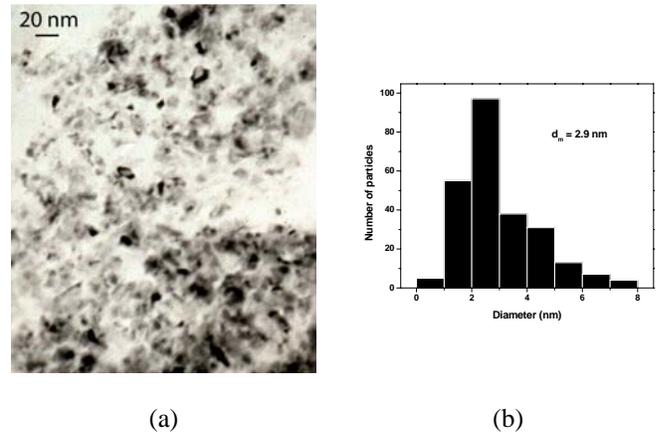
Phase Imaging is a powerful extension of TappingMode™ AFM. It provides nanometer-scale information about surface structure and properties often not revealed by other SPM techniques. By mapping the phase of the cantilever oscillation during the TappingMode scan, phase imaging goes beyond simple topographical mapping to detect variations in composition, adhesion, friction, viscoelasticity, and numerous other properties. Phase

imaging was used in both sample TiO₂ and Ni/TiO₂, in the first one no phase contrast was found that means the presence of one compound in the second, phase contrast become visible as is shown in the Figure 3c.

Mapping of different components in composite materials, as Ni/TiO₂ sample, is show in the Figure 3c. In this figure Ni nanoparticles appears as light areas in the phase image. The size of this light areas or Ni nanoparticles is of an average of 14 nm. The particle distribution of Ni in the TiO₂ is almost homogeneous.

3.3 TEM and HRTEM studies

Specimens for TEM analysis were prepared by the slow evaporation of a drop of the colloidal solution after the purification process deposited onto a holey carbon covered copper grid. TEM experiments were performed on a JEOL-1200 EX electron microscope, operating at 120 KV. TEM micrographs of Ni nanoparticles before mixing with TiO₂ solution, revealed the formation of nickel nanostructures with an average size of 10 nm (Figure 4).



(a)

(b)

Figure 4. TEM images of Ni nanoparticles prepared from Ni(COD)₂ in THF in presence of 5 equiv. 1,3-diaminopropane.

The microstructure of the Ni/TiO₂ film was observed using a JEOL 2200FS field emission gun (FEG) TEM equipped with in-column energy filter (Omega Filter because of shape of the electronic trajectories) to produce a high-end, optimally configured TEM for energy filtered imagery. Figure 5 shows HRTEM micrographs of Ni/TiO₂ film.

Figure 5(a) shows Ni/TiO₂ sample with particle size less than 15 nm. This parameter was measured by digital micrograph software of GATAN Company. The grain size is very similar of that obtained by AFM. The Figure 5(b) shows HRTEM micrograph at higher magnification clearly shows the lattice planes of monocystal TiO₂. Interplanar spacings *d* were determined by FFT, the space between the lattice plane was 0.352 nm which corresponds well to *d*

value of (101) plane for anatase, which is in agreement with the theoretical data.

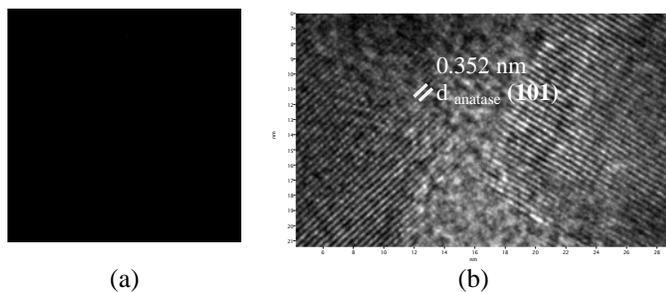


Figure 5. TEM (a) and HRTEM (b) of Ni/TiO₂ film micrographs calcined at 400 °C for 3 h at two different magnifications.

3.4 Photocatalytic Evaluation

In order to evaluate the photocatalytic activity of TiO₂ and Ni/TiO₂ films, the photodegradation of ethanol was performed at 25 °C under UV illumination.

For the visible light experiment, the sample was illuminated with a 25 W mercury 2 lamps (Trojans) at a distance of 10 cm from the glass reactor.

100 g of glass spheres films were placed in a 30 cm long and 5 cm diameter cylindrical air-filled static glass reactor with a pyrex window by degrading a mixture composed by ethanol (1.05x10⁻⁴ gmol/min), water (molar ratio EtOH/H₂O= 0.3) and N₂ (20 ml/min, Praxair) pretreated at 100 °C. The obtained products (hydrogen and acetaldehyde) were analyzed using gas chromatography using a Varian Star 3400-TCD chromatograph equipped with Porapak Q column (3 m).

The photocatalytic properties with the presence of Ni nanoparticles reached values of 90, 550 and 586 μmol after 12, 25 and 40 min the exposure time. TiO₂ and Ni/TiO₂ films exhibited 23 and 40 % degradation of ethanol respectively after the same time of UV exposure.

Conclusions

In this study, we prepared nanocrystalline TiO₂ and Ni/TiO₂ composite thin films by sol-gel dip-coating technique. XRD results showed that these films exhibited anatase phase.

The photocatalytic properties of the prepared thin films were evaluated by degrading ethanol under UV. It was observed that Ni/TiO₂ system calcined at 400 °C for 3 h show high catalytic activity on the photodegradation of ethanol.

In the absence of Ni nanoparticles, the degradation of ethanol was dramatically lower reaching a value of about 23 % about 12 min after the lighting of the light source. Pure Ni/TiO₂ film showed 44 % degradation of ethanol after 40 min of UV exposure.

In order to extend the utility of Ni/TiO₂ material further studies related to TiO₂ and Ni/TiO₂-based nanocomposites at different calcinations temperatures are now in progress.

The hydrogen production rate observed in the Ni/TiO₂ system, reveal very efficient photocatalytic ethanol degradation.

References

- [1] C. He, Y. Yu, X. Hu, A. Larbot, *Appl. Surf. Sci.* 200, 239-247, 2002.
- [2] A. Fujishima, K. Honda, *Nature*, 238, 37-38, 1972.
- [3] B. O'Regan, M. Gratzel, *A low-cost, Nature*, 353, 737-740, 1991.
- [4] A. L. Linsebigler, G. Lu, J. T. Yates, *Chem. Rev.* 95, 735-758, 1995.
- [5] S. Castillo, T. Lopez, *Appl. Catal., B. Environ.* 15, 203-209, 1998.
- [6] I. M. Arabatzis, T. Stergiopoulos, M. C. Bernard, D. Labou, S. G. Neophytides, P. Falaras, *Appl. Catal., B. Environ.* 42, 187-201, 2003.
- [7] C. C. Chang, J. Y. Chen, T. L. Hsu, C. K. Lin, C. C. Chan. *Thin Solid Films*, 516, 1743-1747, 2008.
- [8] M. Yoshinaga, H. Takahashi, K. Yamamoto, A. Muramatsu, T. Morikawa, *J. Colloid and Interface Science*, 309, 149-154, 2007.
- [9] D.E. Zhang, X.M. Ni, H.G. ZhengT, Y. Li, X.J. Zhang, Z.P. Yang, *Mater. Lett.*, 59, 2011– 2014, 2005.
- [10] Y. Zhao, E. Yifeng, L. Fan, Y. Qiu, S. Yang., *Electrochim. Acta* 52, 5873–5878, 2007.
- [11] C. Bittencourt, A. Felten, J. Ghijsen, J.J. Pireaux, W. Drube, R. Erni, G. Van Tendeloo, *Chemical Physics Letters*, 436, 368–372, 2007.
- [12] H. He, R.H. Heist, B.L. McIntyre, T.N. Blanton, *Nanostructured Materials*, 8, 7, 879-888, 1997.
- [13] X.G. Li, T. Murai, A. Chiva, S. Takahashi, *J. Appl. Phys.* 86, 1867-1873, 1999.
- [14] E. Verrelli, D.Tsoukalas, K. Giannakopoulos, D. Kouvatso, P. Normand, D. E. Ioannou. *Microelectronic Engineering*, 84, 1994–1997, 2007.
- [15] N. Cordente, M. Respaud, F. Senocq, M. J. Casonove, C. Amiens and B. Chaudret, *Nano Lett.* 1, 565-568, 2001.
- [16] H. Takahashi, Y. Sunagawa, S. Myagmarjav, K. Yamamoto, N. Sato, A. Muramatsu, *Mater. Trans.* 44, 2414-2416, 2003.
- [17] S. Myagmarjav, H. Takahashi, Y. Sunagawa, K. Yamamoto, N. Sato, E. Matsubara, A. Muramatsu, *Mater. Trans.*, 45, 2035-2038, 2004.
- [18] Z. Yuan, J. Zhang, B. Li, J. Li., *Thin Solid Films*, 515, 7091-7095, 2007.
- [19] F. D. Duminica, F. Maury and R. Hausbrand, *Surface and Coatings Technology*, 201, 9349-9353, 2007.
- [20] Petr O. Vasiliev, Bertrand Faure, Jovice Boon Sing Ng and Lennart Bergström, *Journal of Colloid and Interface Science*, 319, 144-151, 2008.
- [21] P.V. Kamat, *J. Chem. Rev.*, 93, 267-300, 1993.