

Fluorescent effects of silica xerogel induced by incorporation of chard leaves extracts and ZnO nanoparticles

J.M. Guajardo-Pacheco*

Departamento Físico Matemáticas, Facultad de Ingeniería, Universidad Autónoma de San Luis Potosí
Álvaro Obregón 64, 78000 San Luis Potosí, S.L.P.
México

G. Ortega-Zarzosa, J R Martínez

Facultad de Ciencias, Universidad Autónoma de San Luis Potosí
Álvaro Obregón 64, 78000 San Luis Potosí, S.L.P., México

(Recibido: 26 de septiembre de 2007; Aceptado: 21 de febrero de 2007)

This work studies the effect of incorporating fluorescent organic extracts and oxide zinc nanoparticles in silica xerogel composites prepared by the sol-gel method, under different condition of preparation, which confer different optical and structural characteristics to product. The samples at room temperature and heat-treating at annealing temperature were studied using infrared spectroscopy, fluorescence, X-ray diffraction and differential temperature analysis.

Keywords: Sol gel; Fluorescence; Chlorophyll; Zinc oxide nanoparticles

1. Introduction

The sol gel process is a versatile method for making ceramic and glass materials based in incorporation of particles embedded in inert matrixes such SiO_2 with specific properties, which are related with the structure of the forming composites materials [1]. The SiO_2 glasses prepared by the sol gel method have been used experimentally as supporting substrates to organic and inorganic molecules [2]. They specially have been used in three-dimentional constructions, in which “guests” (e.g., atomic clusters, organic molecules) are dispersed in the framework voids [3].

The higher plants are a efficient systems to absorb and transfer the energy through photosynthetic apparatus. This situation can be used to take advantage of preparing materials based in extract of plants for eventually design efficient optical and electro optical materials, such as sensors, laser, etc. [4]. ZnO is one of transparent conducting oxide materials that have properties as high optical transparency in the visible and near-infrared region. Due to these properties ZnO is a promising material for electronic or optoelectronic applications such as solar cell (anti-reflecting coating and transparent conducting materials), gas sensors, liquid crystal displays, heat mirrors, etc., [5]. This is why, it is necessary to understand the structural and fluorescence change of extracted components of leaves and nanoparticles of ZnO embedded in silica xerogel matrix, as well as the interaction with the inorganic matrix under heat treatment in which the matrix goes from gel to glass transition, and then correlate with optical and structural properties.

In this work two kinds of materials were prepared under different conditions. Both samples have extract of chard leaves using ethanol as solvent and nanoparticles of ZnO . The first sample was catalized with HCl (sample A), and the second sample was prepared without catalyst (sample

B). Each sample gets different optical and structural characteristics to product.

2. Experimental method

The method to obtain the chlorophyll is be crudely extracted from frozen chard leaves by simple grinding and mixing them with ethanol solvent. In order to obtain the organic and inorganic composites embedded in xerogel matrix, a precursor material composed of tetraethylorthosilicate (TEOS), water, nanoparticles of ZnO suspension and ethanol with extract of chard leaves was prepared. The ethanol to TEOS and water to TEOS molar ratios were 4:1 and 11:1, respectively. This composition has been proved to give good quality SiO_2 coating. These quantities correspond to a high water/TEOS ratio, needed to enhance the hydrolysis to assure a close amorphous structure for the as-prepared SiO_2 powder [1]. The TEOS was dissolved in the ethanol by extract magnetic stirring for 15 min and then the water was added to the ethanol TEOS solution to form the starting material. However, with the finality to incorporate extract into xerogel matrix was necessary to add a catalyst, for that reason the sample A were prepared with HCl and the sample B without catalyst with the finality of comparison. For the sample A the HCl to TEOS molar ratio was 0.06:1.

Fluorescence spectrum was obtained using CCD, Ocean Optics, Inc SF 2000, argon laser of 532 nm and filter HNF-532-1.0. The X-ray diffraction (XRD) patterns were obtained using a GBC Difftech MMA diffractometer. It was used the nickel filtered $\text{Cu K}\alpha$ ($\lambda=1.54$ Å) radiation. The infrared (IR) spectra were recorded in a Fourier transform infrared (FT-IR) spectrometer Nicolet system model Avatar 360 using the transmittance mode, for which 0.05 g of powder sample was mixed with 0.3 g of KBr . Differential thermal analyzer (DTA) measurements were carried out in a TA instruments system, model Q600, at

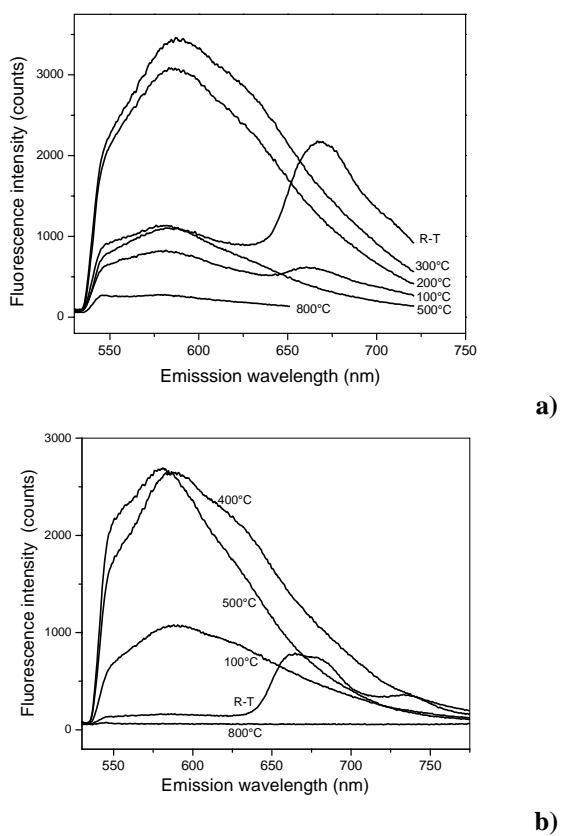


Figure 1. Fluorescence spectrum for (a) samples catalyzed with HCl and (b) without catalyst.

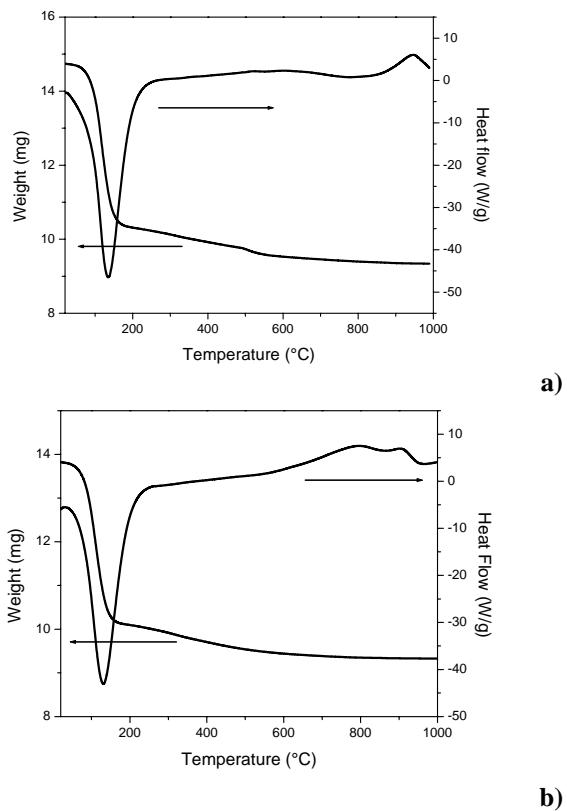


Figure 2. Heat Flow and weight loss curves of chlorophyll species and nanoparticles of ZnO embedded in a silica matrix for (a) sample A, and for (b) sample B.

constant rate of 20°C/min inside DTA analyzer in nitrogen atmosphere up to 1000°C.

3. Results and discussion

Depending on condition preparation two different products were obtained. When HCl was used as catalyst we obtained initially just one phase and the product is a compact glass whereas without HCl catalyst two phases were obtained and the product was a porous powder, in the sense that are formed open structures includes polymerized species predominantly with oligomers [6]. In order to investigate the structural and fluorescence change, both set of samples were heat-treated at a range from 100°C to 800°C and then was irradiate with 532 nm laser, the fluorescence results obtained are shown in figure 1.

The sample A present the typical chlorophyll *a* fluorescence spectrum up to 100°C [5], whereas, the sample B just to room temperature show fluorescence spectrum in which the main contribution is the chlorophyll *b* [5,7]. In both samples, after the decomposition of chlorophyll system, some fluorescents species was to be formed emitting in the 550-650 nm range. In the sample A that species begin emitting at room temperature, then, the fluorescence intensity decrease at sample heat-treated at 100°C, in upper temperatures the chlorophyll decompose and the samples only emitting in the range 550-650 nm. From 100°C to 300°C the fluorescence intensity increase, in such range and present it's maximum of fluorescence intensity at 300°C. In samples heat-treated upper 300°C the fluorescence intensity decrease whereas the heat-treatment increased; however, exist at high temperatures (800°C). In the sample B the chlorophyll species decompose in temperature lower than 100°C, and in this heat-treated temperature the sample begin to fluoresce in the range 550-650 nm increasing the fluorescence intensity when the heat-treated temperature increased showing the maximum of fluorescence intensity at 500°C, disappearing after this temperature. In samples of silica xerogel embedded only with extract of leaves we observed that the maximum intensity fluorescence in the range 550-650 nm is obtained at samples heat-treated at 200°C, whereas in samples of silica xerogel embedded only with ZnO nanoparticles fluorescence is absent. We don't know which kind of components were created, further investigations are necessary. However, according with previous results, the chlorophyll species begin decomposing at temperatures above 200°C after water elimination, in according with the endothermic peak in figure 1. Its decomposition conduces to the formation of magnesium oxide species, organic compound that produce quenching centers. In samples only with incorporation of extract of spinach leaves, we obtain brucite layer phase and trioxide of magnesium [6]. The samples show optical absorption in the UV region from 200 nm to 390 nm due to the incorporation of ZnO nanoparticles.

In order to investigate the structural change of this composites, the as-prepared powder were heated at constant rate 20°C/min inside a DTA analyzer in nitrogen

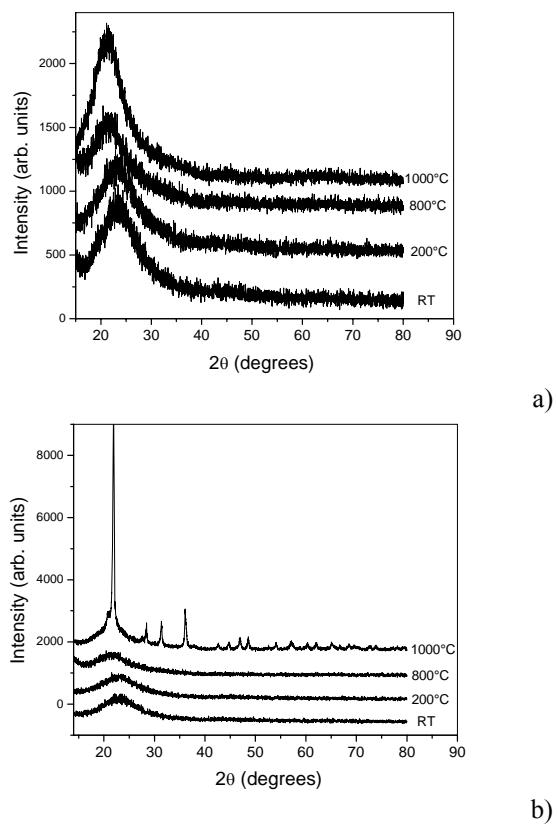


Figure 3. X-ray diffractograms of the chlorophyll-ZnO-containing silica xerogel samples heat-treated at the indicated temperature for (a) sample catalyzed with HCl and (b) without catalyst.

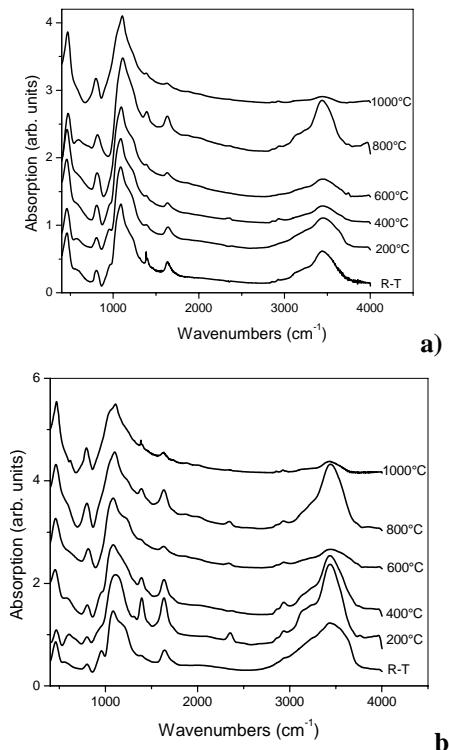


Figure 4. Infrared absorption spectra of the chlorophyll containing silica xerogel samples for (a) sample catalyzed with HCl and (b) without catalyst.

atmosphere up to 1000°C. As shown in figure 2, the analyzed samples display different behaviour.

For the samples A and B, the DTA endothermic peak at 130°C corresponds to partial water elimination accompanied with a drastic loss of percent weight. The comportment of the DTA curves are different at temperatures above 800°C, for the sample B it is observed exothermic peaks at about 800°C and 900°C, associated with partial crystallization of the matrix in form of cristobalite phase, whereas for the sample A only one exothermic peak at about 940°C is present indicating more ordering in amorphous like cristobalite. For this sample the exothermic peak at about 570°C is related with the transformation for the silica xerogel matrix from quartz-like amorphous to low-cristobalite amorphous phase [8]. In the sample B, the exothermic peak at 900°C can be related to the crystallization of SiO₂ as cristobalite phase. Figure 3 shows the X-ray diffractograms for the prepared samples. Embedded in amorphous silica xerogel the chlorophyll species decomposed and interacted with the silica matrix promoting the formation of new fluorescent species. Using both results, DTA and X-ray diffraction, we can see that in samples heat-treated below 1000°C, only the broad peak corresponding to the SiO₂ gel is showed, the main feature common to all these patterns is a broad peak located at the left part of the diffractogram. As the treatment temperature is raised, this band suffers a slight shift to lower values of diffraction angle 2θ. For the room-temperature (R-T) sample the position of the peak centre is around 23° and by heat-treating the sample at 800 °C the position is shifted to 21°. It is important to mention that cristobalite has its main diffraction peak at 21°. Many authors have correlated the shift of the broad peak, induced by heat-treatment, to the structural conformation change of the silica network [9-13], but to temperatures up to 1000°C the sample A show a behaviour amorphous and the sample B has very different behaviour and we can observe peaks corresponding to the cristobalite phase.

The infrared absorption in the range of 400 to 4000 cm⁻¹ is shown in Figure 4. The main band is located at about 1089 cm⁻¹ for the sample A and at 1099 cm⁻¹ for the sample B. In the former sample this band is enhanced, increasing in the annealing temperature. In addition, the presence of free surface silanols bands (3724 cm⁻¹) SiOH and an absorption band at the range 1270-1560 cm⁻¹ for sample heat-treated at 1000°C is associated with a combination of vibrations of the CH species. The presence of this band at high temperature for the sample B, indicated among the presence of organic compound, is an evidence of the linear structure for the matrix [14], in addition the shoulder from 600 cm⁻¹ to 1000°C has been interpreted as a change of structure, according to X-ray results.

For sample A the band at the range 1270-1560 cm⁻¹ for sample heat-treated at 1000°C is almost incorporated to the main stretching band, has been interpreted as due to the formation of a chain-or ringlike structure.

The weak band for the sample B at the range from 1250 to 1550 cm⁻¹ and 2800-3000 cm⁻¹, and it is diminished by heat-treatment at temperatures higher than 200°C,

indicating the change of the OR groups due to the chlorophyll decomposition. In the same time the Si-O-Si chain in formation are terminated by OH species, as an evidence of the linear character.

4. Conclusions

In summary, this work shows that the chlorophyll in combination with ZnO nanoparticles embedded in amorphous silica xerogel decomposed and interacted with the silica xerogel promoting the formation of fluorescent aggregates. In presence of HCl as catalyst the denaturation of chlorophyll photosystem is carried out at temperature higher than without HCl catalyst, this is possible because the extract is encapsulated into the matrix and without catalyst is just a mixed. In addition, the HCl delays the crystallization to temperatures up to 1000°C and without HCl the crystallization of the matrix is to 1000°C.

Among the optical properties the incorporation of ZnO nanoparticles in the compound retarded the devitrification of the silica xerogel matrix as occur when only extract of spinach leaves are incorporated to the silica matrix [6]. Their incorporation promote the optical absorption in the UV region and promote the fluorescence in the range from 550 nm to 650 nm at higher temperatures than sample with only incorporation of extract leaves.

References

- [1] J.R. Martínez, F. Ruiz, Y.V. Vorobiev, F. Pérez-Robles and J. González-Hernández, *J. Chem. Phys.*, **109**, 7511 (1998)
- [2] L. Persaud, A.J. Bard, A. Campion, M.A. Fox, T.E. Mallouk, S.E. Webber and J.M. White, *J. Am. Chem. Soc.*, **109**, 7309 (1987)
- [3] W. Bard and T. Mallouk, in *Electrodes modified with clays, zeolites, and related microporous solids*, in *Molecular Design of Electrodes Surfaces*, edited by R.W. Murray, (Willey 1992) p 271
- [4] Quan Chang Li, Vageesh Kuman, Yan Li, Haitao Zhang, Tobin J. Marks, E. and Robert P.H. Chang, *Chem Mater.* **17**, 1001 (2005)
- [5] A. Vázquez-Durán, C. Araujo-Andrade, G. Martínez-Castañón, G. Ortega-Zarzosa, Facundo Ruiz, and, J.R. Martínez, *J. Sol-Gel Sci & Techn.*, **39**, 223 (2006)
- [6] J.R. Martínez, G. Martínez-Castañón, G. Ortega-Zarzosa, J.A. de la Cruz-Mendoza, S.A. Palomares-Sánchez, and, Facundo Ruiz, *Research Letters in Materials Science*, vol. 2007, Article ID 23018, 5 pages, (2007), doi:10.1155/2007/23018
- [7] J.M. Briantais, C. Vernotte, G.H. Krause, and E. Weiss, In *light emission by plants and bacteria*. (1986, Academic Press, New York,) pp.539-583
- [8] J.R. Martínez, S. Palomares-Sánchez, G. Ortega-Zarzosa, Facundo Ruiz, and, Y. Chumakov, *Mat. Lett.*, **60**, 3526 (2006)
- [9] J. Majlinc and P. Znasik, *J. Mater. Res.*, **10**, 2411 (1995)
- [10] J. Ikushima, T. Fujiwara, and K. Saito, *J. Appl. Phys.*, **88**, 1201 (2000)
- [11] K. Oh-Yun, S. Hak-Sik, and C. Sang-Won, *Chem. Mater.*, **12**, 1273 (2000)
- [12] H. Isobe, I. Tokunaga, N. Nagai, and K. Kaneko, *J. Mater. Res.*, **11**, 2908 (1996)
- [13] J.H. Jean and T.K. Gupta, *J. Mater. Res.*, **8**, 2393 (1993)
- [14] G. Ortega-Zarzosa, C. Araujo-Andrade, M.E. Compeán-Jasso, J.R. Martínez, and F. Ruiz, *J. Sol-Gel Sci & Techn.*, **24**, 23 (2002).