Textural, structural and electrical properties of TiO$_2$ nanoparticles using Brij 35 and P123 as surfactants

Dora Solís$^1$, Enrique Vigueras-Santiago$^1$, Susana Hernández-López$^1$, Antonio Gómez-Cortés$^2$, Manuel Aguilar-Franco$^2$ and Marco Antonio Camacho-López$^1$

$^1$ Facultad de Química, UAEM, Paseo Colón y Tollocan 50,000, Toluca, México
$^2$ Instituto de Física, UNAM A. P. 20–364 México DF 01000 México

E-mail: dasolis@uaemex.mx

Received 19 July 2007
Accepted for publication 29 January 2008
Published 12 June 2008
Online at stacks.iop.org/STAM/9/025003

Abstract

The effect of the use of the triblock copolymer Pluronic P123[(PEO)$_{20}$(PPO)$_{70}$(PEO)$_{20}$, Aldrich] and the non-ionic polyoxyethylene-lauryl ether Brij 35 as surfactants on the textural, structural and electrical properties of nanosized TiO$_2$ is analyzed in this work. The as-obtained samples were thermally treated at 400 $^\circ$C to eliminate the surfactant, promote dehydroxylation and crystallize the sample. The TiO$_2$ samples were characterized by thermal analysis, N$_2$ physisorption, x-ray diffraction analysis, micro-Raman spectroscopy and scanning electron microscopy. To evaluate the TiO$_2$ electrical features, I–V data were obtained. The x-ray diffraction results show that in the chemical synthesis using surfactants, the crystallite size is smaller than that of the commercial sample. The Raman spectroscopy results clearly indicate that, when P123 is used, the anatase phase of TiO$_2$ is obtained, whereas when Brij 35 is used a mixture of the anatase and brookite phases is obtained. The specific surface area and crystallite size of the TiO$_2$ prepared as indicated above are higher and smaller, respectively, than the corresponding properties found in commercial TiO$_2$. The I–V plot showed a nonlinear behavior of the nanosized TiO$_2$. The samples obtained with P123 showed the best electrical conductivity.

Keywords: nanosized titania, self-assembly technique, Brij 35, P123, electrical resistance

1. Introduction

Titanium oxide (TiO$_2$) has been extensively studied owing to its wide range of applications which include photocatalysis, heterogeneous catalysis, energy storage and as white pigments, solar cell components, corrosion-protective coatings and optical coatings [1–5]. Titanium dioxide can be synthesized in three crystalline phases: rutile, brookite and anatase [6]. Titanium dioxide in the anatase crystalline phase is one of the most studied materials for photocatalysis. Among the various metal oxides that can be used in gas sensors, only those materials based on stannic oxide and titanium oxide have been widely manufactured and utilized [7]. The aforementioned background justifies the need to improve the properties and features of these oxides in order to obtain a more efficient material for gas sensing purposes. In addition, there is as yet no report on the effect of the specific surface area of these materials on gas sensing performance. It has been reported that the use of surfactants in the self-assembly technique in obtaining titania materials inhibits crystallite growth, preventing crystallites from being sintered rapidly and also promotes the increase in specific surface area [8].

The use of nanosized materials is continuously increasing, mainly owing to the unique and interesting properties that these materials have. The physical and chemical properties of these materials strongly depend on...
the size of the particles that are formed. It has been reported that materials composed of a collection of nanosized particles have high specific surface areas and homogeneous pore diameter distributions. There are several techniques for the synthesis of nanostructured materials in the literature [9]. One of the chemical methods of obtaining nanoparticles is based on the use of polymers as structure-directing agents, which is well known as a self-assembly technique. In self-assembly, atoms, molecules, particles and other building blocks organize themselves into functional structures as driven by the energy of the system [10–12]. Some researchers have studied the changes in structure and the functionality, and reported the effects of the shape and size control of TiO$_2$ nanoparticles with surfactants on the photocatalytic applications of TiO$_2$ [11]. Other researchers have explained why nanoparticles are obtained using neutral surfactant templates, the reasons being the high surface areas have explained why nanoparticles are obtained using neutral surfactants on the structure-directing agents and the titanium tetraisopropoxide as the titanium source. Commercial TiO$_2$ (Baker, 99.9% purity) was used for comparison purposes and designated C-3.

2.1. Sample preparation

Nanosized TiO$_2$ was prepared by hydrothermal self-assembly, as reported in the literature [8], using the triblock copolymer Pluronic P123 [(PEO)$_{20}$(PPO)$_{70}$(PEO)$_{20}$, Aldrich] and the nonionic polyoxyethylene-lauryl ether Brij 35 as structure-directing agents and the titanium tetraisopropoxide as the titanium source. Commercial TiO$_2$ (Baker, 99.9% purity) was used for comparison purposes and designated C-3.

2.1.1 Pluronic P123. 2 g of Pluronic (P123) was dissolved in a mixture consisting of 1 ml of water and 5 ml of 2 M HCl solution under vigorous stirring at 40 °C. Then 13 ml of titanium tetraisopropoxide (Aldrich, 97%) was added dropwise to the solution. The mixture was stirred at 40 °C for 24 h and then aged at 100 °C for 72 h without stirring. The solid product was recovered by filtration in vacuum, washed with deionized water, and air-dried at room temperature. To eliminate the surfactant and promote the dehydroxylation and crystallization, the sample was thermally treated in static air at 400 °C for 4 h. The resulting sample was designated C-1.

2.1.2. Brij 35. 16 g of Brij 35 was dissolved in water with stirring at 80 °C and then 13 ml of titanium tetraisopropoxide (Aldrich, 97%) was added according to the procedure reported to obtain CeO$_2$ [10]. The mixture was stirred for 24 h and then aged without stirring at 70 °C for 72 h. The solid product was recovered by filtration in vacuum, washed with distilled water and air-dried at 70 °C for 12 h. Thermal treatment was performed in static air at 400 °C for 4 h; this sample was designated C-2.

2.2. Sample characterization

The samples were characterized by thermogravimetric analysis (TGA), N$_2$ physisorption, x-ray diffraction (XRD) analysis and micro-Raman spectroscopy. The thermograms of the as-synthesized samples were determined in an equipment SDT Q600 module of TA instruments. The conditions were as follows: nitrogen flow; temperature range, 25–900 °C; and heating rate, 20 °C min$^{-1}$. The N$_2$ adsorption/desorption isotherms were measured with a Quantachrome Autosorb automatic analyzer at liquid N$_2$ temperature (−196 °C). Prior to the experiments, the samples were degassed (P < 10$^{-1}$ Pa) at 200 °C for 3 h approximately. Specific surface area was calculated by the Brunauer–Emmet–Teller (BET) method ($S_{BET}$). Pore volume (Vp) was determined by nitrogen adsorption at a relative pressure of 0.99 and the pore size distributions were obtained from the isotherm desorption branches by the Barret–Joyner–Halenda (BJH) method using the Kelvin equation. The XRD patterns were recorded in the 20 ≤ 2θ ≤ 80° range using a Bruker diffractometer using CuK$_\alpha$ radiation ($\lambda = 0.15406$ nm). Mean crystal lattice size was obtained by the Rietveld structure refinement method. The Raman spectra of the samples were collected in a micro-Raman system (Labram HR-800 of Jobin–Yvon–Horiba). The system was equipped with a He–Ne laser ($\lambda = 632.8$ nm) and an Olympus BX-41 microscope. Scanning electron microscopy (SEM) was carried out in a Jeol JSM 5600-LV microscope.

2.3. Electrical characterization

The electrical characterization of the samples was carried out using the circuit shown in schematic diagram 1. The voltage ($V_m$) in the sample (S) was measured when the potential ($\varepsilon$) in the range of 0–100 V was applied; a resistance $R$ of 10.5 M$\Omega$ was used. An electrometer Keithley model 6517A was used to apply potential ($\varepsilon$) and monitor voltage ($V_m$). Disks with a diameter of 1.2 cm and a thickness of 1 mm obtained by pressing the TiO$_2$ powders at 200 kg cm$^{-2}$ were
Figure 1. Thermogravimetry of sample synthesized with P123 surfactant.

used. Electrodes (silver paint) on the two opposite sides of the disks were impressed. The current was calculated using equation (1) which is the solution of the electrical circuit.

\[ I = \frac{\varepsilon - V_m}{R}. \]  

(1)

3. Results and discussion

3.1. Thermogravimetric analysis

Figure 1 shows a TGA diagram corresponding to the sample synthesized using the P123 surfactant. An important weight loss starting at 250°C can be seen. When the temperature reached 350°C, the weight loss became quite constant. The weight loss was due to surfactant elimination and dehydroxylation. A similar TGA profile was obtained for the sample synthesized with Brij 35 (not shown here). Taking into account the thermal analysis results, the as-synthesized samples were thermally treated at 400°C for 4 h to obtain titania mainly in its anatase crystalline phase.

3.2. N₂ physisorption

Table 1 shows the specific surface areas (S_{BET}), mean pore diameters (D_p), pore volumes (V_p) and crystallite sizes of the C-1, C-2 and C-3 samples. As can be seen in this table, the C-1 and C-2 samples have specific surface areas higher than that of the C-3 sample (commercial titania). These results were obtained because of the reduction in crystallite size from 64 nm (C-3) to 8–9 nm (C-1 and C-2), which was promoted by the use of the surfactants (samples C-1 and C-2 samples); a significant increase in surface area was obtained with crystallite size reduction. The thermally treated TiO₂ showed high specific surface areas when the surfactants were used to synthesize the material, being 194–201 m² g⁻¹ for C-2 and C-1, respectively, whereas the C-3 sample showed a lower specific surface area (12 m² g⁻¹). From N₂ physisorption isotherms 2c and 2b corresponding to the C-1 and C-2 samples, respectively, (figure 2), and from the form of the hysteresis reported in the literature, firstly by Brunauer and then by Leofanti et al [15, 16], we can assume interparticle voids in the mesoporous range. Isotherm 2a corresponding to the commercial TiO₂ sample indicate interparticle voids in the macroporous range. Figure 3 shows the mean pore diameter obtained from the BJH from the desorption branch, from which voids between crystallites can be estimated, which are homogeneous for samples C-1 (figure 3(c)) and C-2 (figure 3(b)); in the C-3 sample, it is evident that the interparticle voids are mostly heterogeneous (figure 3(a)). It is important to consider the surfactant as a structure-directing agent, which allows us to obtain a mean homogeneous pore diameter.

3.3. X-ray diffraction analysis

Figure 4 shows the XRD profiles of the C-3, C-2 and C-1 samples. The pattern in figure 4(a) shows diffraction peaks for commercial TiO₂. All the peaks were indexed with the standard from the Joint Committee of Powder Diffraction Standards (JCPDS 21-1272) and correlated to the reflection
planes of the anatase phase. The intensity and full width at half maximum (FWHM) of the diffraction lines indicate that the material has a high degree of crystallinity. The diffraction patterns in figures 4(b)–(c) correspond to the C-2 and C-1 samples, respectively. In the C-2 sample, the peaks are mainly assigned to the anatase crystalline phase and there are some diffraction lines that indicate the brookite crystalline phase (*), which are identified from the DRX profiles indexed with the JCPDS 29-1360 and its composition percentage was calculated by the Rietveld refinement method to be 44.7% for this C-2 sample. One can see that the FWHM is wider and the intensity is lower than that of the C-3 sample. This is due to the nanosized particles of the TiO₂. The decrease in the intensity of the diffraction lines is related to the presence of nanosized crystallites. Similar results have been found by Zhang et al [8]. The crystallite size of the samples was obtained by the Rietveld refinement method. The crystallite sizes are nanometric as can be seen in table 1 with values between 6.2 and 4.4 nm for the C-1 and C-2 samples, respectively; the crystallite size for the commercial sample (C-3) was 98 nm.

3.4. Micro-Raman spectroscopy

Figure 5 shows the Raman spectra for the C-3, C-2 and C-1 samples in the range of 190–800 cm⁻¹. The Raman spectrum 5(a) for the commercial sample consists of several peaks located at 196, 396, 516 and 639 cm⁻¹, which can be assigned to the anatase phase [6]. Spectrum 5(c) corresponding to the synthesized sample C-1 does not present the peak at 196 cm⁻¹ and the intensity of the anatase bands is lower than the one seen in the commercial material. In the case of sample C-2 (spectrum 5(b)), in addition to the anatase phase peaks, one can observe new bands at 212, 246, 325, 367, 455 and 587 cm⁻¹. These bands can be assigned to the crystalline phase known as brookite, as previously reported [6], according to the observed x-ray diffraction profile of this sample. These features indicate that the use of Brij 35 (sample C-2) induces the formation of a mixture of crystalline phases, composed of anatase and brookite.

Figure 6 shows the Raman spectra of the C-3, C-2 and C-1 samples in the range of 90–200 cm⁻¹. In this region,
a peak related to the $E_g$ vibrational mode appears and it is assigned to the anatase phase. For the commercial sample, the peak is centered at 143.5 cm$^{-1}$. In the cases of the C-2 and C-1 samples one can note the following: a frequency redshift, a reduction in peak intensity and a broadening of the peak (FWHM increases). These features are related to the crystallite size of the nanosized titania and oxygen vacancies [17]. The redshifts of the peaks are similar for the C-2 and C-1 samples, which indicate that the crystallite sizes are of the same order for both samples. This is in good agreement with the crystallite sizes reported in table 1. Several authors have reported the Raman features of nanosized TiO$_2$. For instance, Scepanovic et al [18] have studied the effect of crystallite size and nonstoichiometry on the Raman spectrum of TiO$_2$ nanopowders.

3.5. Scanning electron microscopy

Figure 7 shows a set of SEM images corresponding to C-1(c), C-2(b) and C-3(a). One can observe morphological differences between samples synthesized using surfactants and the titania commercial sample. Figure 7 (a) shows semi-spherical aggregates of particles, however, the particle size cannot be observed by this technique. The micrograph in figure 7(b) showed some differences in aggregates morphology, which could be assumed to be a different form of these aggregates. Figure 7(c) shows aggregates with semispherical aggregates that seem to conform with particles smaller than those observed in figure 7(a).

3.6. Electrical characterization

Figure 8 shows a plot of the current–voltage relationship for the C-1, C-2 and C-3 samples. Note that the sample works as a resistance and a capacitor at the same time. From this point of view, the measured voltage ($V_m$) is the charge voltage of a capacitor and the calculated current is the current passing through the sample. Thus, it can be observed that the sample load in C-1 is less than those in C-2 and C-3, but at the same time C-1 is the most conductive. The current in sample C-2 crosses the curve in sample C-3 at 2.6 V indicating that C-2 is more resistive than C-3. Considering that the crystallite sizes and oxygen vacancies are similar for the C-1 and C-2 samples, the electrical behavior of the C-2 sample with respect to those of the C-1 and C-3 samples can be attributed to a mixture of crystalline phases. The I–V curves for the three samples do not follow Ohm’s law. This is in good agreement with the results for TiO$_2$ published by Earle [19], who has studied in detail the electrical conductivity of TiO$_2$. 

Figure 7. SEM images of samples: (a) commercial (C-3), (b) Brij35 (C-2) and (c) P123 (C-1).

Figure 8. I–V curves for samples: (a) commercial (C-3), (b) Brij35 (C-2) and (c) P123 (C-1).
4. Conclusions

It can be concluded that the use of surfactants helps to obtain materials with higher specific surface areas, which are preformed by small and homogeneous crystallite sizes. The TiO$_2$ materials synthesized using the surfactants Brij 35 and P123 presented nanometric crystallite sizes of 4.4 and 6.2 nm, respectively. The XRD and Raman spectroscopy features of the nanosized materials reported in the literature also corroborate the results of this work. Both powder XRD analysis and Raman spectroscopy allowed us to identify a mixture of crystalline phases, anatase and brookite, in the sample obtained when Brij 35 was used. The increase in specific surface area was expected since nanometric crystallite sizes were obtained, which promoted an increase in the electrical conductivity of the bulk material, evaluated preliminarily through I–V curves and from results of the capacitor experiments. The purity of the anatase crystalline TiO$_2$ phase seemed to be a factor that influences the electrical properties of nanosized TiO$_2$, since the sample C-2 had showed a different behavior and it is composed of nanoparticles as well; however, this sample had the brookite crystalline phase. It can be concluded that nanosized TiO$_2$ could be a good candidate material for gas sensing probes when it contains mainly the anatase crystalline phase.

Acknowledgments

This work was supported by the following projects: UAEM-2349/2006 and 2215/2006. D Solis thanks CONACyT for financial support (Programa de Consolidación Institucional). We thank Physicist Roberto Hernández Reyes for his valuable help in obtaining the SEM images.

References

[1] Colón G, Maicu M, Hidalgo M C and Navio J A 2006 Appl. Catal. B: Environ. 67 41
[2] Amezcue J C, Lizama L, Salcedo C, Puente I, Domínguez J M and Klímová T 2005 Catal. Today 107–108 578
[3] Wawzyzniaik B, Waldemar A and Tryba B 2006 J. Photoenergy 1
[4] Barborini E, Bongiorno G, Forleo A, Francioso L, Milani P, Kholmanov I N, Piseri P, Siciliano P, Taurino A M and Vinatry S 2005 Senors Actuators B 111–112 22
[5] Prabir K D and de Lucia M F 2006 Senors Actuators B 115 1
[6] Tompsett G A, Bowmaker G A, Cooney R P, Metson J B, Rodgers K A and Seakins J M 1985 J. Raman Spectrosc. 26 57
[7] Ishokura K and Watson J 1994 The Stannic Oxide Gas Sensor: Principles and Applications (Boca Raton, FL: CRC Press)
[8] Zhang J Z, Zhong-lin W, Liu J, Chen Sh and Liu G 2003 Self-Assembled Nanostructures (Dordrecht: Kluwer Academic/Plenum Publishers)
[9] Fendler J H and Tian Y 1998 Nanoparticles and Nanostructured films: Preparation, Characterization and Applications (New York: Wiley-VCH) p 429
[10] Solís D, Gómez-Cortes A and Díaz G 2006 Scientific Bases for the Preparation of Heterogeneous Catalysts, Series: Studies in Surface Science and Catalysis (Amsterdam: Elsevier Science) p 363
[11] Liao D L and Liao B Q 2007 J. Photochem. Photobiol. A 187 363
[12] Zhu J, Tay B Y and Ma J 2006 Mater. Lett. 60 1003
[13] Marie-Paule P 2003 Nat. Mater. 2 145
[14] Schwarzenbacher R, Kriebsbaum M, Amenitsch H and Laggner P 1998 J. Phys. Chem. B 102 9161
[15] Brunauer S, Deming L S, Deming E and Telle E 1940 J. Am. Chem. Soc. 62 1723
[16] Leofanti G, Padovan M, Tozzola G and Venturelli B 1998 Catal. Today 41 207
[17] Parker J C and Siegel R W 1990 J. Mater. Res. 5 1246
[18] Šćepanović M J, Grujić-Brojin M U, Dohčević-Mitrović Z D and Popović Z V 2006 Mater. Sci. Forum 518 101
[19] Earle D M 1942 Phys. Rev. 61 56