Room temperature sintering of polar ZnO nanosheets: III-Prevention

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Abstract

In this study, the coating of high specific surface area stainless steel wire mesh-supported ZnO with a monolayer of silica was investigated with the aim of preventing the room temperature sintering of the polar ZnO sample (75% specific surface area loss in two months in the presence of moisture, oxygen or light). This research study is the logical conclusion of previous works by the authors in which the room temperature sintering of polar ZnO was detected and analyzed for the first time (DOI: 10.1039/c7cp02306e and DOI: 10.1039/c7cp02307c). The ZnO surface was modified by inducing a substitution reaction between 3-aminopropyltriethoxysilane (APTES) and surface hydroxyls, followed by a low-temperature calcination step to produce a monolayer of silica (2 atom%) that would provide stability to the ZnO surface. The textural and structural characteristics of the protected material hardly differ from those of freshly calcined (unprotected) ZnO samples, and remain unchanged for long storage periods. This is due to the action of the silica coating, which causes an increase in the number of oxygen interstitials and a decrease in the amount of oxygen vacancies. The combination of these factors provokes the immobilization of the Zn interstitials, whose mobility is responsible for the room temperature sintering of unprotected ZnO. The efficiency of the polar ZnO as a sacrificial template remains unchanged in the presence of silica. Additionally, the photocatalytic activity of the protected ZnO sample in the continuous photodegradation of methylene blue shows a slight improvement compared to that of the unmodified sample calcined at the same temperature. Moreover, losses of Zn during the reaction diminished.

Keywords: silica coating, polar ZnO, specific surface area, room temperature sintering, photocatalysis

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Introduction

As we have recently proved, the surface of polar ZnO nanoparticles calcined at low temperature (210°C) is unstable. It undergoes significant change during the room temperature storage of the particles in the presence of moisture, oxygen or light, in a process that lasts around two months [1, 2]. During this period of time, the specific surface area of the zinc oxide decreases from 115 to 35 m²·g⁻¹. The mechanism governing this phenomenon has been described in the preceding parts of this work [1, 2]. Briefly, it starts with the molecular adsorption of water, which takes place on Zn atoms close to oxygen vacancies on the (100) surface, where H₂O dissociates to form two hydroxyl groups and to heal one oxygen vacancy. This process triggers the migration of interstitial Zn atoms towards the outer surface of the polar region. Upon reaching the polar region, the interstitial Zn atoms show up on the (00 $\bar{1}$) surface where, among other actions, they can displace terminal hydroxylated Zn atoms on the O-terminated polar plane. What were previously interstitial Zn atoms now gradually occupy the mesopores, with interstitial oxygen being used to build up a O sublattice until total occupation of the narrow mesoporosity is achieved [2].

Typically ZnO is synthesized in the form of 1D (i.e. nanorods), 2D (i.e. nanosheets) or 3D (i.e. nanoflowers) structures with specific surface areas ranging from 6 to 75 m² g⁻¹ [3]. These structures usually have a low polarity, which is probably why no signs of room temperature sintering in these materials have ever been detected. Very high specific surface area (over 100 m² g⁻¹) polar ZnO structures, such as those described in our previous works [4, 5], are less common. Nevertheless, the specific surface area of mesoporous ZnO materials is of prime importance for many physicochemical and electrochemical applications [3, 6, 7], as well as for the development of new materials [4]. Thus, the high surface area polar ZnO catalyst which was the object of our previous studies [1, 2] is both an excellent photocatalyst [5] and the precursor of a variety of single and mixed metal oxide nanocatalysts of high specific surface area [4]. As a photocatalyst, the effect of its specific surface area on catalytic activity is not evident, since the activating light only illuminates the outermost

surface of the catalyst and the adsorption of the contaminant depends both on the point of zero charge of the material and on the pH of the solution [5]. In its role as sacrificial template [4] the effect of the loss of specific surface area on the properties of the synthesized metal oxide nanoparticles is still unknown. In any case, a method to prevent the room temperature sintering of the polar surface of ZnO nanoparticles has become a requisite before use. Because this sintering phenomenon has only recently been detected, no protection methods have been investigated to date. However, some methods to prevent other unwanted phenomena are described in literature. For example, the silica coating of ZnO nanoparticles is considered to be an effective way to minimize photocorrosion [8-10]. In this study, we hypothesize that a thin homogeneous silica coating might also prevent the room temperature sintering of ZnO, though it needs to be carried out in such a way that (i) the efficiency as a sacrificial template of the material is preserved and (ii) the reduction of ZnO photocatalytic activity is avoided. Vu *et al.* [8] achieved an homogeneous distribution of silica on the surface of ZnO nanoparticles via dip-coating with polysiloxane emulsions that led to a reduction in photocorrosion to almost zero, but at the expense of a significant decrease in photoactivity (at best higher than 50%) and to a high loss of specific surface area (around 65%), probably due to a SiO₂ multilayer formation. Siddiquey *et al.* [9, 11] and other research groups [12, 13] described a surface-modification approach consisting of the covalent attachment of 3-aminopropyltriethoxysilane (APTES) to the surface of ZnO nanoparticles to incorporate an amine-reactive functionality onto the surface of ZnO for various purposes, including the reduction of its photocatalytic activity [11]. What is interesting about these works, compared to the present study, is that (i) the ethoxyl groups of the APTES molecules react via hydrolysis and condensation with the hydroxyl groups on the ZnO surface, converting the Zn-OH bonds into Zn-O-Si bonds [11] and (ii) calcination of the functionalized material (not performed in the works referred to above) would probably lead to the formation of a silica monolayer that might affect the photoactivity of the material less than a thicker layer [8]. Hydroxyl groups on the polar surfaces of ZnO are temporary

doors through which the interstitial Zn atoms enter the mesopores of the material [2], and therefore their replacement by Zn-O-Si bridges would provide a way to close these doors.

With this in mind, the aim of the present work is to propose a method of protecting the ZnO surface, based on the use of APTES, in order to prevent the room temperature sintering of the material. The coating must not decrease either the efficiency of the zinc oxide as a sacrificial template or its catalytic activity in the photodegradation of contaminants, as occurs with freshly calcined unprotected ZnO material. It is expected that an additional advantage of the method proposed will be a greater resistance against photocorrosion of the protected material. The surface changes introduced by the protection method will be analyzed by applying different spectroscopic techniques, and the results will be compared to those obtained from a study of the unprotected ZnO surface [1, 2].

Experimental

Synthesis of stainless steel wire mesh-supported ZnO

All the chemicals used in this work were of analytical grade and did not require additional purification. The standard method of synthesis of a stainless steel wire mesh-supported ZnO monolith is described elsewhere [1, 2]. Briefly, a stainless steel wire mesh (SSWM) provided by CISA (36 μm wire diameter and 42 μm screen opening) was washed with HNO_3 (4 M) (from J. T. Baker) at 60°C for 4 hours and then with isopropyl alcohol in an ultrasonic bath for 10 minutes (from J. T. Baker). Dihydrated zinc acetate and urea powder (both from Sigma-Aldrich) were dissolved together in 100 mL of deionized water to obtain solutions of urea and Zn^{2+} in molar concentrations of 1.00M and 0.05M, respectively. Next, 85-100 mg of Triton™ X-100 (from ChemLab NV) and 3 cm^3 of 5 ppm aqueous solution of monohydrated methylene blue (from Sigma Aldrich) were added to the synthesized solution [5]. The pH of the solution was then adjusted to 4.88 using a GLP21 pHmeter (Crison) by adding an appropriate amount of acetic acid (from J.T. Baker) aqueous solution

(1.2 M). The 5x5 cm² wire mesh was placed in a Teflon™ autoclave (120 cm³ volume) that was then filled with the synthesis solution. The Teflon™ autoclave was then sealed and placed in a furnace at 80°C for 23 h to allow the growth of hydrothermal ZnO. After this time, the ZnO coated-wire mesh was taken out of the precursor solution and washed with deionized water several times. To eliminate the poorly adhered active phase, the sample was immersed in an ultrasonic bath for 10 minutes and then vacuum-dried at 60°C for at least 30 minutes. Finally, with only a few exceptions, the sample was calcined at a temperature of 210°C for 1 hour in air to obtain the standard-ZnO sample (20.35 ± 2.21 wt.%). This sample will be referred to as U-ZnO-T_C (U stands for Unprotected and T_C for the selected calcination temperature).

Protection method

The U-ZnO-210 sample was immersed in a Teflon™ autoclave (50 cm³) containing a solution composed of 1 mL of 3-aminopropyltriethoxysilane (APTES; from Sigma-Aldrich) and 50 mL of ethanol (puriss. p.a.; from J.T.Baker). The solution was prepared under an inert atmosphere in a glove bag to prevent the APTES from decomposing. The autoclave was then sealed and placed in a furnace at 80°C. After 4 hours, the sample was taken out of the solution, rinsed several times with ethanol to remove any APTES excess and vacuum-dried at 60°C for at least 30 minutes. Finally, the sample was calcined in air for 1 hour at a given temperature [T_C = 25 (for the uncalcined samples), 250 or 550°C]. The protected monolith will be referred to as P-ZnO-T_C (P stands for protected and T_C for the selected calcination temperature). To allow the room temperature sintering of the protected samples to be evaluated and characterized over long periods of time, the samples were left on open Petri dishes and kept under the laboratory light on worktop tables (*unprotected storage* [2]).

Sacrificial template synthesis of stainless steel wire mesh-supported CeO₂

In order to assess the effect of the protection method on the efficiency of the ZnO-based material as a sacrificial template, samples of SSWM-supported CeO₂ were fabricated by using the protected and unprotected ZnO as templates via a synthesis method based on that described by Vu and Marbán [14]. Briefly, U-ZnO-210, U-ZnO-250 and P-ZnO-250 templates (either freshly calcined or stored at lab conditions for a long period of time) were immersed in plastic flasks containing water solutions of cerium nitrate (0.045 M; provided by Sigma-Aldrich) in quantities that allowed the initial Ce/Zn atom ratio to be fixed at a value of 2. The molarity of the solution was selected in order to maximize the exchange of cerium (see Figure S1 in the Supplementary Information). The closed flasks were subjected to shaking at RT in an orbital shaker for 5 days. Afterwards, the samples were taken out of the flasks and washed with deionized water, vacuum-dried at 60°C for 30 min and calcined in air at 250°C for 2 hours.

Characterization techniques

Unless otherwise stated, the default protected sample used in all characterization techniques was P-ZnO-250. The morphology and metal distributions of the samples were studied on a scanning electron microscope (SEM, FEI Quanta FEG 650 model) and attached to an energy dispersive X-ray (EDX) detector. The X-ray diffraction (XRD) patterns of the samples were recorded on a Bruker D8 Advance instrument operating at 40 kV and 40 mA using Cu K α radiation (λ = 0.15406 nm). The crystal size values were estimated from the (100) peak of the XRD pattern by means of Scherrer's equation. The BET specific surface area was calculated via the single-point method by means of N₂ physisorption at -196 °C in a Micromeritics Autochem II chemisorption analyzer. N₂ adsorption-desorption isotherms of selected samples were performed at -196 °C in a Micromeritics ASAP 2020 analyzer. The pore size distribution (PSD) was calculated from the N₂ adsorption isotherms by means of the Kruk-Jaroniec-Sayari method [15]. UV-VIS diffuse reflectance spectroscopy measurements were carried out to determine the bandgap energy value in a Shimadzu UV-2460

spectrophotometer equipped with an integrating sphere. Raman spectra from 200 to 800 cm^{-1} were obtained at room temperature on a T64000 System (Horiba) using as excitation source the 514.53 nm line of an Ar ion laser and excitation times of 30 seconds. All the reported peak areas, positions and widths are the result of Gaussian fitting. Ex-situ X ray photoelectron spectroscopy (XPS) was carried out on a Specs spectrometer, using Mg-K α or Al-K α (30 eV) radiation emitted from a double anode at a power of 50 W. The binding energies of the resulting spectra were corrected employing the binding energy of adventitious carbon (284.6 eV) in the C1s region. The backgrounds were corrected using Shirley baselines. All the analyzed regions were deconvolved by means of mixed Gaussian-Lorentzian functions (90:10). The quantitative analyses were based on atomic sensitivity factors stored in the CasaXPS database (v2.3.12Dev6). Transmission Fourier Transform Infrared Spectroscopy (FTIR) spectra of the samples both as ZnO powder compressed into discs with KBr and as mesh-supported ZnO, were recorded from 500 to 4000 cm^{-1} on a Nicolet Magna IR 560 spectrometer fitted with a DTGS absorbance detector. In the case of the ZnO powder samples, the KBr discs were crushed after each analysis for further storage and pressed again just before the next analysis. The analysed regions were deconvolved with the aid of Gaussian functions. To determine the point of zero charge (pH_{pzc}) the pH drift method was used [5, 16]. Briefly, 50 cm^3 aqueous solutions of NaCl (0.01 M; from Sigma-Aldrich) with pH values in the 4-10 range were prepared by adding either HCl (0.1 M; from J.T. Baker) or NaOH (0.1 M; from Sigma-Aldrich). Samples of around 50 mg of zinc oxide were added to each solution at room temperature and vigorously shaken for 2 days. The initial and final pH values were measured using a GLP21 pHmeter (Crison). The intersection of the curves formed by both sets of values plotted against the initial pH served to determine the pH_{pzc} of the analyzed sample. The amount of methylene blue adsorbed by the SSWM-supported catalysts at different pH values was evaluated by introducing catalyst samples in 50 cm^3 aqueous solutions of MB (10 ppm) at specific pH values, adjusted by adding small amounts of HCl (0.1 M) or NaOH (0.1 M). The solutions were mechanically shaken for one day to ensure

equilibrium adsorption. The concentration of MB before and after equilibrium adsorption was analyzed using an UV-Vis spectrometer (Shimadzu UV-2401PC) from the absorbance at 664 nm.

Continuous photocatalytic activity tests

Continuous operation photodegradation experiments were performed in a flow-through reactor described in detail in [5]. Briefly, a 10 ppm MB aqueous solution was magnetically stirred and air bubbled in a 2 L amber glass bottle. The methylene blue cationic dye was obtained from Sigma-Aldrich and was used as received. In a typical reaction experiment, the liquid stream ($20 \text{ cm}^3 \cdot \text{h}^{-1}$) was continuously fed from the MB reservoir into the reactor with the aid of a four-channel peristaltic pump (Ismatec Ecoline VC-MS/C44-12 with Pharmed BPT tubing, 0.25 mm i.d.). The reactor consisted of a polystyrene filter holder in which the filter was replaced by a disc-shape catalyst (37 mm diameter, $\sim 112 \text{ }\mu\text{m}$ thickness). The level of solution covering the disc was kept to a minimum ($\sim 1 \text{ mm}$) by using a transparent quartz disc (1 mm thickness) as a top cap. The system was irradiated from the top using a UV light source with an irradiance of $10 \text{ mW} \cdot \text{cm}^{-2}$ (Opsytec Dr Gröbel RM-12 radiometer). Prior to irradiation, it was necessary to establish an adsorption-desorption equilibrium of MB on the catalytic disc under darkness (minimum time of 1 hour). The liquid stream exiting the reactor was collected in test tubes at controlled time intervals using a Frac-920 fraction collector (GE Healthcare Life Sciences). The collected samples were analyzed in an UV-vis spectrometer (Shimadzu UV-2401PC) and an ICP-MS analyzer (Agilent 7700x model) in order to evaluate the MB concentration (absorbance at 664 nm) and Zn^{2+} concentrations, respectively. In one specific case, a reactivation step was performed after the reaction. This step consisted in pumping deionized water for about 5 hours to the reactor while the UV light source continued to illuminate the catalyst disc. The reaction-reactivation process was repeated four times in order to evaluate the extent of catalyst deactivation.

Discussion of results

Effect of silica protection on room temperature sintering

The U-ZnO-210 samples produced showed an average ZnO yield of 20.4 ± 2.2 wt.%. When the APTES protection coating was applied to the U-ZnO-210 surface to obtain P-ZnO-T_C, a minute loss of ZnO mass was observed, resulting in a final yield of 19.8 ± 2.1 wt.%. SEM images of U-ZnO-210 and P-ZnO-250 samples are shown in Figures 1A and 1B, respectively. The oriented polar ZnO nanosheets [1, 9] can be clearly seen in both samples. The morphological characteristics of the aligned ZnO nanosheets were not affected by the presence of silica. EDX analysis of the surface of P-ZnO-250 yielded a silicon concentration of 3.3 ± 1.0 atom%, considering only the Zn and Si atoms. The silicon percentage obtained by ICP-MS analysis was, as expected, somewhat lower (2.0 ± 0.6 atom%). EDX mapping proved that the silicon was homogeneously distributed on the ZnO surface.

As reported in a previous work [2], and the results of which are shown in Table 1, a freshly calcined U-ZnO-210 sample (210°C) has a specific surface area of $\sim 115 \text{ m}^2 \cdot \text{g}^{-1}$. The P-ZnO-250 sample has an almost identical initial surface area value ($115.4 \text{ m}^2 \cdot \text{g}^{-1}$). In addition, the N₂ physisorption isotherms of both samples proved to be identical (Figure 2A), indicating that the silica coating process had no effect on the textural characteristics of the freshly calcined material. As can be seen in Table 1, P-ZnO-25 has a slightly lower BET surface area than the calcined P-ZnO-250 sample, $\sim 83 \text{ m}^2 \cdot \text{g}^{-1}$, due to the pore volume being occupied by aminopropyl ligands. Interestingly, the P-ZnO-550 sample has a much higher specific surface area ($\sim 65 \text{ m}^2 \cdot \text{g}^{-1}$) than the unprotected sample calcined at considerably lower temperatures ($27 \text{ m}^2 \cdot \text{g}^{-1}$ at 350°C and $24 \text{ m}^2 \cdot \text{g}^{-1}$ at 450°C [5]), indicating that silica coating also exerts a positive effect on the ZnO resistance to thermal sintering.

The evolution of specific surface area on a ZnO mass basis with time for the protected and unprotected samples during storage under laboratory conditions is shown in Figure 3. After unprotected storage for over two months, the specific surface area of the U-ZnO-210 sample decreased to $33 \text{ m}^2 \cdot \text{g}^{-1}$ (72% surface area loss), with most of the surface reduction taking place during the first two weeks [1]. In contrast, the specific surface area loss of P-ZnO-250 was much lower and more gradual, reaching a maximum value of only 19.3% after 56 days (Figure 3). These results confirm the role silica coating plays in mitigating the room temperature sintering of ZnO. The N_2 physisorption isotherms on a ZnO mass basis for the P-ZnO-250 and U-ZnO-210 samples, both freshly calcined and after 40 days under lab conditions, are shown in Figure 2. All isotherms are of type III in the Brunauer classification [17, 18], with a hysteresis loop typical of mesoporous materials. As reported in a previous work [1], the pore size distribution (PSD) of U-ZnO-210 (insets in Figure 2) changed from a bimodal PSD (with two maxima at 6 and 68 nm) to a unimodal PSD (with one maximum at 69 nm) after 40 days under laboratory conditions. In contrast, the protected sample retained its bimodal PSD, with only a slight variation in the position of the maxima (6 and 128 nm at 0 days, and 6 and 65 nm after 40 days) and a more significant decrease in the amount of physisorbed N_2 , though this had only a slight effect on the resulting specific surface area (Figure 3). It must be considered that the second maximum of the PSDs spans over a high pore diameter range, and this is the reason for the difference between the results obtained at both storage times (Figure 2). What really counts is that the mesoporous fraction, with a maximum at 6 nm, retains this value during the storage period due to the protective role of the silica coating.

Figure 4 shows the XRD spectra in the $30\text{-}38^\circ$ range of P-ZnO-250 at different storage times. All the diffraction peaks are well indexed to hexagonal ZnO (JCPDS card no. 36-1451) with characteristic peaks (crystal planes) at 31.8° (100), 34.4° (002) and 36.2° (101). The high purity of the synthesized ZnO samples is confirmed by the well-defined diffraction peaks. Moreover, no impurities were detected by SEM-EDX. The P-ZnO-250 sample displayed a similar pattern to that of U-ZnO-210

(dashed line) but, whereas the peak intensity ratios were clearly affected by the storage time in the case of the unprotected sample [1], the morphology and crystal structure of the ZnO nanosheets in P-ZnO-250 did not experience any significant change during 44 days of storage. This can be appreciated more clearly from the inset plot of Figure 4. It can be seen that the crystal size evaluated by applying Scherrer's equation varied during the storage time within a very small range of 9.1-9.5 nm, whereas the unprotected material underwent a notable increase to 14 nm in only 15 days (Table 1). The same observation applies to the I_{002}/I_{100} ratio, where there is only a small variation in the 0.55-0.58 range in the case of the protected sample. These results demonstrate that the silica coating is effective in preventing the room temperature sintering of the ZnO nanosheets, and that their textural and morphological properties remain unchanged.

Surface spectroscopic characterization

In order to elucidate the protection mechanism, the P-ZnO-250 sample was subjected to spectroscopic characterization. The results of this examination will be compared to of our previous work on an unprotected sample [2], where it was concluded that the sintering phenomenon is closely connected with the polarity of the material, with surface hydroxyls, oxygen vacancies (V_O) and interstitial zinc atoms (I_{Zn}) playing an important role. In line with this procedure, the present work analyzes P-ZnO-250 both in powder form, where the polar faces are mainly exposed [1], and supported on the mesh, where the non-polar edges are mainly exposed [1]. In other words, in this work “ZnO powder” is synonymous with “polar ZnO” and “mesh-supported ZnO” is synonymous with “non-polar ZnO”. To obtain the powder, groups of ZnO nanosheets were gently scratched away from the wire mesh surface with a brush and then disaggregated in a mortar. Unless otherwise stated, a sample must be assumed to be in the form of mesh-supported ZnO.

Raman spectra obtained for P-ZnO-250 samples, both as mesh-supported ZnO and as a powder, after different storage times (0, 7, 12, 30, 44 days) are shown in Figure S2. A detailed description of each

of the eleven peaks necessary for the deconvolution is reported elsewhere [2] and in the Supplementary Information. Raman peaks #2, #10 and #11 are the most relevant peaks in this work, and they are attributed to hydroxyls, Zn interstitials and oxygen vacancies, respectively [2]. According to the sintering mechanism described in the preceding work [2], the massive movement of interstitial Zn atoms within the ZnO structure towards the mesopores explains why the mesopores eventually become blocked. Figures 5A and 5B illustrate the variation in concentration of Zn interstitials on the polar and non-polar faces of ZnO for both the unprotected (Fig. 5A) and protected (Fig. 5B) materials. Contrary to what occurs in the unprotected sample, the concentration of Zn interstitials remains practically constant in the protected sample during the entire storage period. Similarly, the amount of oxygen vacancies in the protected material (Fig. 5D) remains essentially unaffected (only a small increase with the storage time is detected in the more polar zones) and is significantly lower than that in the unprotected material (Fig. 5C). Hydroxyl groups associated to zinc atoms on the surface of the protected sample are also present in lower levels than in the unprotected sample (Figs. 5E and 5F). It is unclear, however, whether some of the zinc hydroxyls have been neutralized by the action of APTES, turning the Zn-OH bonds into Zn-O-Si bonds [11], or the dissociative chemisorption of water has been reduced by the lower availability of oxygen vacancies [2]. Although variations are less pronounced in the protected sample, the same trends affecting the levels of hydroxyls and oxygen vacancies over time are maintained in comparison to the U-ZnO-210 sample (Figs 5C to 5F), which is consistent with the sintering mechanism previously proposed [2]. In any case, the lower level of hydroxyls and oxygen vacancies, together with a smaller variation in their concentration during storage (Figs. 5D and 5F) is what eventually reduces drastically the transfer of Zn interstitials outside (Figure 5B).

XPS analyses of the protected samples, both as a powder and as mesh-supported ZnO, were performed at five different storage times (0, 7, 12, 30 and 44 days) using both Mg-K α and Al-K α sources. The Al-K α source offers the possibility of deeper layer analyses than the Mg-K α source, so

that some depth profiles can be revealed. The C1s, O1s, Zn2p_{3/2} and Si2p regions were used to quantify the surface composition of the samples and were deconvolved to determine the different types of bond. Corrections for charging effects, adventitious carbon, adventitious oxygen and adventitious silicon (contributions resulting from the adhesive tape used to hold the samples) were performed in order to establish the true surface composition of all analysed samples. A detailed description of the different XPS peaks and correction procedures are included in the Supplementary Information, together with all the deconvolved spectra (Figure S3-S8) and surface composition values (Tables S1 and S2). The most relevant data for the purpose of the present discussion are shown in Tables 2 and 3.

The binding energy values did not show any excessive difference when compared to those of the freshly calcined U-ZnO-210 sample. The incorporation of silica onto the P-ZnO-250 surface was confirmed by the appearance of two peaks in the Si2p region at 104.5 eV (Si-O-Si bonds [19]) and at 106.5 eV (water adsorbed on silica, SiOH₂⁺ [19]). As can be seen in Tables 2 and 3, the initial amount of total silicon (over the basis of only the Zn and Si atoms) was 4.6 atom% (Mg-K α source) or ~3.7 atom% (Al-K α source), regardless of the polarity of the analyzed surface. These values are consistently higher than those supplied by EDX (3.3 atom%) and ICP-MS (2.0 atom%) and demonstrate that the silicon is homogeneously dispersed over the ZnO surface as a monolayer. Therefore, assuming that a monolayer of SiO₂ occupies ~2270 m² per gram of SiO₂ (SiO₂ density = 2.3×10²² molecules cm⁻³; SiO₂ molecule height = 0.262 nm) then, the fraction of the ZnO surface occupied by the SiO₂ monolayer would be at least 0.5-0.6 (in fact, it should even be higher since the XPS technique underestimates the surface contribution of the superficial elements with respect to the bulk elements). However, during the storage process, the Si-O-Si fraction decreases, and this decrease is more marked on the polar surface. In principle, this could be associated to the progressive adsorption of moisture that produces SiOH₂⁺, though the percentage of this species does not seem to be affected (Tables 1 and 2). On the other hand, it should be borne in mind that the ZnO surface,

though fairly stabilized, is still experiencing a slight decrease during storage (Figure 3) which affects the dispersion of silica. This might be also the reason why the decrease in silica is more marked on the polar ZnO surface, where the ZnO interstitials emerge [2]. In any case the variations are only minor and they may also be the result of experimental error.

As can be observed in Table 2, zinc hydroxyls on the polar surface of the protected sample are present in a lower proportion than in the unprotected sample and their concentration remains more or less constant during storage, thus confirming the results obtained by Raman analysis (Figure 5). Such consistency, however, is rather surprising, considering that the number of hydroxyls, though low, is still substantial. This suggests that the SiO₂ monolayer is covering a large part of the ZnO surface, and partially prevents the formation of hydroxyls on the non-polar ZnO surface during storage (Table 3). Nevertheless, according to our calculations, 40% at most of the ZnO surface remains uncovered and is therefore available for the dissociative adsorption of water. We suggest that the formation of hydroxyls is taking place on the non-polar surface as a consequence of the combination of two factors: namely, the high initial level of surface hydroxyls [considering that most of the ZnO surface is covered by SiO₂, the amount of hydroxyls is as high as half that of the highly sintered unprotected surface (Table 3)] and the low level of oxygen vacancies in comparison to that of the unprotected sample (Figures 5C and 5D) since for the dissociation of H₂O from a Zn atom on the polar surface to occur, an adjacent oxygen vacancy must be eliminated [2]. But, what is the cause of the low level of oxygen vacancies in the protected material? As can be seen in Tables 2 and 3, the combined amounts of oxygen vacancies (V_O) and interstitial oxygen (I_O) in the protected material are much higher than in the unprotected sample. To reconcile these results with those of Raman (Figures 5C and 5D) it must be concluded that the majority of defects evaluated in the O1s region for the protected sample are oxygen interstitials, resulting from the addition of silica. A similar phenomenon was observed for silicon doped zinc oxide thin films [20]. The reason for such increase is not clear yet. The results presented above indicate that the addition of silica causes both an increase in I_O defects (Tables 2 and

3) and a decrease in V_O defects (Figures 5C and 5D), and that this is why the interstitial Zn atoms are less mobile in the protected material than in the unprotected sample (Figures 5A and 5B), in accordance with the sintering mechanism previously proposed [2]. The O/Zn ratios shown in Tables 2 and 3 are heavily affected by these facts. On the polar face of the protected sample the presence of a high concentration of zinc interstitials (Figs. 5A and 5B) is more conspicuous than the increase in I_O defects, which results in a net decrease in the O/Zn ratio with respect to that of the unprotected sample (Table 2). On the other hand, the non-polar face experiences a significant increase in the O/Zn ratio after the incorporation of silica (Table 3), which may be partly due to the greater number of I_O defects, but also to the parallel formation of zinc vacancies.

FTIR spectra of the U-ZnO-210 and P-ZnO-250 samples are shown in Figures S9 and S10. The presence of dissociatively bound H_2O was confirmed by two absorbance bands at 1630 and 3400 cm^{-1} [21]. The magnitude of these peaks depends heavily on the thermal drying of the sample. The small bands between 2800 and 3000 cm^{-1} are associated to the C-H stretching vibrations of residual alkane groups [22] resulting from the calcination of the hydrozincite precursor, and these were drastically reduced after the protection treatment as a response to the double calcination. The narrow peak at 1384 cm^{-1} is also attributed to residual carboxylates from the hydrozincite calcination [2]. The main differences between the protected and the unprotected samples are easily appreciated in the 750 - 1300 cm^{-1} range. In the case of the unprotected sample (Figure S9), the bands in this range were assigned to a small fraction of hydroxycarbonates quickly formed as a result of exposure to moist air [2]. These peaks disappeared in the protected sample (Figure S10) giving way to a well-defined double peak (Figure 6), in slightly different wavelength positions for the polar and non-polar surfaces (~ 900 and $\sim 1010\text{ cm}^{-1}$ for the polar face and ~ 885 and $\sim 970\text{ cm}^{-1}$ for the non-polar face). The low wavelength peak can be assigned to the Si-O-Zn bending vibration [11, 23, 24], which would suggest that SiO_2 has been grafted onto the ZnO particles, whereas the second peak corresponds to the Si-O-Si antisymmetric stretching mode [25, 26]. The area ratio of the first peak to the second

peak was 30/70 on the polar surface and 56/44 in the case of the mesh-supported ZnO, regardless of the storage time. This confirms that a silica monolayer was successfully incorporated on the surface of the ZnO particles, and that the formation of hydroxycarbonates from the moist air was avoided.

Effect of the silica monolayer on the sacrificial template accelerated hydrolysis synthesis of stainless steel wire mesh-supported CeO₂

To evaluate the effect of the protection method on the performance of the SSWM-supported ZnO material as a sacrificial template, samples of SSWM-supported CeO₂ were fabricated as described in the Experimental section using both the protected and unprotected ZnO samples as sacrificial templates. The results obtained are shown in Table 4. As can be seen from the table, the values of CeO₂ yield and specific surface area improved slightly when the protected material was used as template, especially after a long storage time. Nevertheless, the CeO₂ properties remained practically unchanged regardless of the template initially used (unprotected or protected, freshly calcined or after a long storage time). From the results, it can be concluded that the performance of the sacrificial template is not altered by the presence of a protective layer of silica.

Photocatalytic activity under continuous operation

The Kubelka–Munk method was employed to determine the band gap of the different materials (Figure 7 and Table 1). As a direct wide band gap semiconductor (~3.30 eV), ZnO is an attractive photocatalyst for reaction under UV irradiation. As shown in Table 1, the silica-coated ZnO samples calcined at low temperature (P-ZnO-25 and P-ZnO-250) present the same band gap values (~3.30 eV) as the freshly-calcined U-ZnO-210 sample. The slight decrease in band gap in P-ZnO-550 (Table 1) is a consequence of the slightly improved light adsorption in the visible region with respect to the samples calcined at low temperature (Figure 7) in a way that is comparable to

what we previously observed for the unprotected samples [5]. This would lead one to expect a better photoactivity in the visible region of the samples calcined at high temperature.

The photocatalytic activity under UV light of P-ZnO-25, P-ZnO-250 and P-ZnO-550 was compared to that of the U-ZnO-210 and U-ZnO-250 samples. To this end, the catalysts were tested in the photodegradation of aqueous methylene blue (MB) solutions performed in continuous operation experiments, as described in [5] and in the Experimental section of this work. The photocorrosion resistance of the photocatalysts was evaluated by assessing the loss of ZnO after reaction. The results of the MB conversion during ~17 h (6×10^4 s) experiments are presented in Table 5 and Figure 8. Blank experiments were conducted to evaluate the MB conversion either in the absence of light (adsorption; 2-6% MB conversion) or in the absence of catalyst (photolysis; 4.4% MB conversion); the average conversion levels are also displayed in Figure 8. Based on the results shown in the figure, both the protected and unprotected photocatalysts behave in a similar way, revealing that the silica layer does not have a negative impact on the photoactivity. In fact, comparison of the catalysts calcined at the same temperature, shows that P-ZnO-250 slightly improves the photoactivity of U-ZnO-250 (46.2% *versus* 43.0% methylene blue conversion after 17h; Table 5). This result constitutes a great advance in comparison with the results of Vu *et al.* [8] who use the same catalyst. In their work, the silica layer was formed by means of dip-coating with a polysiloxane emulsion, thereby allowing photocorrosion to be reduced to almost zero, but at the expense of a significant photoactivity decrease, which was at best higher than 50%. This decrease in activity has been successfully avoided in the present work. On the other hand, the catalyst calcined at 550°C (P-ZnO-550) displays an initial activity that is slightly lower than that of the unprotected catalysts which were also calcined at a high temperature [5]. However, the deactivation rate of the silica-protected catalyst is clearly lower, in a way that the MB conversion after 17h reaction becomes very similar to that of the unprotected catalysts [5].

Table 5 shows the loss of ZnO during reaction (L_{Zn} , wt.%) as a consequence of photocorrosion (partial dissolution of Zn). The absolute amount of Zn^{+2} released into the water by the protected catalysts shows a similar dependence on calcination temperature to that of the unprotected catalysts [5] and, in any case, the losses due to photocorrosion remain exceedingly low (below 2wt.%) when compared to those of other protected ZnO catalysts [8].

The slow deactivation that can be observed in Figure 8 is caused by the accumulation of polycondensed organic compounds on the surface of the material that turn the catalyst blackish, as can be seen in the left photograph in Figure 9, taken after one reaction stage (~20h). These compounds can be removed from the surface of the coated mesh by passing water through the catalyst under UV irradiation for 5 hours [5]. After the reactivation step the catalyst recovers its original aspect (right photograph in Figure 9). Several reaction-reativation cycles were performed with P-ZnO-250 and U-ZnO-250 catalysts (Figure 9). As shown in the figure, both catalysts recover a high activity level after each reactivation step, though P-ZnO-250 is able to maintain a higher and more regular activity. The ZnO losses through photocorrosion decrease over successive cycles, and are always slightly lower with the protected catalyst. In conclusion, the protected catalyst is somewhat more active and also more stable than the unprotected ZnO material. The point of zero charge (pH_{pzc}) of the protected material is also very similar to that of the unprotected ZnO; 7.3 vs. 7.5 (Figure S11). As the pH of the aqueous MB solution is 6.1 (below the pH_{pzc} value), the catalyst surface in contact with the solution is positively charged, which explains the insignificant amount of the cationic dye that is adsorbed by the protected catalyst under darkness (0.23 mg/g). Only when the pH of the solution was increased by the addition of NaOH up to values above the pH_{pzc} , was the adsorption of MB apparent (1.35 mg/g at pH = 9.5). These data confirm that most of the surface of the protected catalyst particles is not in contact with the MB solution, and that the reaction is restricted to the most external non-polar edges of the ZnO nanosheets, as occurs with the unprotected catalyst [5].

Conclusions

In this study, SSWM-supported ZnO was treated with 3-aminopropyltriethoxysilane (APTES) in order to create a monolayer of silica (2 atom%) on the ZnO surface that inhibits the room temperature sintering of ZnO nanosheets. This is possible without compromising the performance of the material either as a photocatalyst or as a sacrificial template for the synthesis of other metal oxides. The protected ZnO nanoparticles maintain the same crystal and textural properties as the freshly calcined unprotected ZnO during aerial exposure for long times. This can be attributed to the action of the silica coating, which leads to an increase in the number of oxygen interstitials and a decrease in oxygen vacancies. These two factors interact to provoke the immobilization of the Zn interstitials, whose mobility is responsible for the room temperature sintering in the unprotected ZnO. The efficiency of the polar ZnO nanosheets as sacrificial template remains unchanged in the presence of silica. Additionally, the photocatalytic activity of the protected ZnO sample in the continuous photodegradation of methylene blue shows a slight improvement compared to that of the unmodified sample calcined at the same temperature. Moreover, the Zn losses during reaction were diminished.

Acknowledgements

The financial support for this research work provided by the Spanish MINECO (CTM2014-56770-R) and FEDER Funds (GRUPIN14-102, Principado de Asturias) is gratefully acknowledged.

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Captions to figures

Figure 1. SEM images of A: U-ZnO-210 and B: P-ZnO-250

Figure 2. N₂ physisorption isotherms for U-ZnO-210 and P-ZnO-250 at A) 0 days of storage time and B) 40 days of storage time. Insets: Pore size distributions of the samples

Figure 3. Evolution of the specific surface area loss with time for the protected catalysts calcined at different temperatures (P-ZnO-T_C) and for the unprotected material (U-ZnO-210)

Figure 4. XRD spectra at different storage times for P-ZnO-250. Dashed line: spectrum for the freshly calcined U-ZnO-210 sample. Inset: variation of d_{XRD} and I_{002}/I_{100} with storage time for the protected material

Figure 5. Evolution of the Raman peak fractions with storage time for powder ZnO (polar) and mesh-supported ZnO (non-polar) samples: (A) U-ZnO-210 (peak #10), (B) U-ZnO-210 (peak #11), (C) U-ZnO-210 (peak #2), (A') P-ZnO-250 (peak #10), (B') P-ZnO-250 (peak #11), (C') P-ZnO-250 (peak #2)

Figure 6. FTIR spectra for P-Zn-250 (either as powder ZnO or as mesh-supported ZnO), freshly calcined and after 44 days of unprotected storage. Inset: Example of deconvolution

Figure 7. UV-vis diffuse reflectance spectra of the protected catalysts calcined at different temperatures (P-ZnO-T_C) and of the freshly calcined unprotected catalyst (U-ZnO-210)

Figure 8. Evolution of the methylene blue conversion with the reaction time for the protected (P-ZnO-T_C) and unprotected (U-ZnO-T_C) catalysts

Figure 9. Consecutive reaction-**reactivation** cycles for U-ZnO-250 and P-ZnO-250

Tables

Table 1. Structural, textural and optical parameters of the U-ZnO-210 and P-ZnO-T_C samples (18-21 wt.%)

Sample	Crystal size (nm)		BET specific surface area (m ² ·g ⁻¹)		Band-gap (eV)	
	0	60	0	60	0	60
U-ZnO-210	9.4	13.8 (15 days)	115.0	32.0	3.30	3.26
P-ZnO-25	9.5	9.0	82.8	70.2	3.31	3.31
P-ZnO-250	9.2	9.3	115.4	93.1	3.30	3.30
P-ZnO-550	11.4	11.7	64.9	55.2	3.25	3.23

Table 2. XPS results for U-ZnO-210 and P-ZnO-250 samples as a powder at different storage times

Storage Time →		0 days		5 (U) 7 (P) days		12 days		30 days		44 days	
XPS source →		Mg-Kα	Al-Kα	Mg-Kα	Al-Kα	Mg-Kα	Al-Kα	Mg-Kα	Al-Kα	Mg-Kα	Al-Kα
V _O (+I _O) (mol%)	P*	12.5	13.5	14.4	15.2	13.9	15.6	17.4	18.0	22.8	23.4
	U*	0.8	14.7	6.5	17.5	-	-	-	-	19.8	17.0
Hydroxyls in Zn(OH) ₂ (mol%)	P	3.6	3.4	3.8	3.9	4.7	3.6	3.5	4.0	4.0	3.7
	U	7.5	6.1	5.8	2.5	-	-	-	-	2.0	1.5
O ¹ /Zn	P	1.13	1.14	1.28	1.19	1.13	1.13	1.35	1.19	1.33	1.26
	U	1.69	1.62	1.79	1.59	-	-	-	-	3.91	2.95
[V _O (+I _O)]/O ¹	P	0.26	0.27	0.28	0.30	0.28	0.31	0.32	0.35	0.42	0.44
	U	0.01	0.24	0.10	0.29	-	-	-	-	0.25	0.23
OH ² /O ¹	P	0.07	0.07	0.07	0.08	0.10	0.07	0.07	0.08	0.07	0.07
	U	0.12	0.10	0.09	0.04	-	-	-	-	0.03	0.02
Zn(OH) ₂ /Zn	P	0.04	0.04	0.05	0.05	0.05	0.04	0.04	0.05	0.05	0.04
	U	0.10	0.08	0.08	0.03	-	-	-	-	0.05	0.03
Si-O-Si (atom%) ³	P	1.8	1.4	1.5	1.2	1.4	1.1	0.7	0.5	0.1	0.2
SiOH ₂ ⁺ (atom%) ³		2.8	2.3	2.8	2.3	3.1	2.5	2.6	2.6	2.7	1.8

* P: Protected sample; U: Unprotected sample; ¹ excluding oxygen linked to silicon; ² linked to Zn; ³ over the basis of only Si and Zn atoms

Table 3. XPS results for U-ZnO-210 and P-ZnO-250 samples as mesh-supported ZnO at different storage times

Storage Time →		0 days		5 (U) 7 (P) days		12 days		30 days		44 days	
XPS source →		Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α	Mg-K α	Al-K α
V _O (+I _O) (mol%)	P*	21.2	18.3	17.6	17.1	19.8	18.4	23.7	20.3	19.0	17.6
	U*	2.0	8.9	1.5	7.6	-	-	-	-	0.0	4.8
Hydroxyls in Zn(OH) ₂ (mol%)	P	3.5	3.0	3.9	3.1	3.4	3.0	2.9	3.2	3.3	3.2
	U	3.1	2.6	5.8	3.6	-	-	-	-	7.2	5.7
O ¹ /Zn	P	1.66	1.57	1.68	1.58	1.63	1.54	1.74	1.71	1.82	1.71
	U	0.94	1.01	0.96	0.99	-	-	-	-	1.10	1.07
[V _O (+I _O)]/O ¹	P	0.37	0.32	0.30	0.30	0.35	0.32	0.39	0.33	0.31	0.29
	U	0.04	0.18	0.03	0.15	-	-	-	-	0.00	0.09
OH ² /O ¹	P	0.06	0.05	0.07	0.05	0.06	0.05	0.05	0.05	0.05	0.05
	U	0.06	0.05	0.12	0.07	-	-	-	-	0.14	0.11
Zn(OH) ₂ /Zn	P	0.05	0.04	0.06	0.04	0.05	0.04	0.04	0.05	0.05	0.05
	U	0.03	0.03	0.06	0.04	-	-	-	-	0.08	0.06
Si-O-Si (atom%) ³	P	1.8	1.2	1.6	1.1	1.5	1.1	1.0	0.4	0.7	0.5
SiOH ₂ ⁺ (atom%) ³		2.8	2.4	2.8	2.4	3.3	2.9	2.2	1.8	2.8	2.5

* P: Protected sample; U: Unprotected sample; ¹ excluding oxygen linked to silicon; ² linked to Zn; ³ over the basis of only Si and Zn atoms

Table 4. Results of CeO₂ prepared by means of STAH synthesis

Sample	ZnO storage time (days)	Yield (wt.%)	Purity (mol%)	S _{BET} (m ² g ⁻¹)	XRD crystal size (nm)
CeO ₂ (from U-ZnO-210)	0	24.68	89.32	114.9	4.30
CeO ₂ (from P-ZnO-250)	0	26.15	90.63	123.0	3.68
CeO ₂ (from U-ZnO-210)	60	23.90	90.76	103.6	4.13
CeO ₂ (from P-ZnO-250)	60	27.60	84.11	129.1	3.00

Table 5. Results of MB photodegradation in the flow-through reactor for the U-ZnO-T_C and P-ZnO-T_C samples

Sample	W _{ZnO} (mg)	X _{MB} at t=10 ⁴ s (%)	X _{MB} at t=6×10 ⁴ s (%)	L _{ZnO} * (wt.%)
U-ZnO-210	55.4	66.5	58.1	3.6
U-ZnO-250	62.0	54.6	43.0	1.7
P-ZnO-25	43.7	65.2	45.5	0.7
P-ZnO-250	61.1	60.0	46.2	1.6
P-ZnO-550	46.0	50.3	37.8	0.9

*ZnO losses at the end of reaction

Figures

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Figure 8

Figure 9