Cyclodextrins as a Templating Agent in Solvent-Free Kneading- Based Syntheses of Nanosized SnO2 and ZnO

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KEYWORDS

Kneading, cyclodextrins, MOS, semiconductor metal oxides, mechanochemistry

ABSTRACT

INTRODUCTION

In recent years, gas sensors have been increasingly used in industrial production and daily life: efficient, low cost and small-sized sensors are nowadays requested in many fields of applications such as environmental, food or biomedical [REF].

In this context, in the ultra-sensible sensors field there has been a growing interest and diffusion of metal oxide-based semiconductors (MOS): MOS are suitable materials for sensors for their outstanding physical and chemical properties that combine high efficiency, fast response, stability and, last but not least, simple preparation and low cost. [1,2]

In gas sensing applications (and in solar cell and photo-catalysis as well) MOS activity is strongly related to the specific surface area [3,4]. To improve the properties of MOS and, consequentially, to improve efficiency of semiconductor metal oxides-based devices, research is nowadays moving towards nano-sized structures with controllable crystalline phases.

There are many examples of synthetic methods for obtaining ceramic nanoparticles, such us thermal and physical deposition, hydro/solvo-thermal processes[5,6] and, over the last few years, electrospinning (ES) [7–14].

ES is a widespread and relatively simple technique to obtain both micro and nano fibers of polymers usually showing high porosity and high specific surface area [15–17]. Recently[18,19], our research group adopted the procedure of electrospinning of polymeric solutions containing precursors of ceramics, followed by thermal treatment, for the obtaining of ceramic nanofibers.

The addition of an oxide precursors to the ES solutions and a subsequent thermal treatment, above the thermal degradation of the polymer, will ablate the polymer and, at the same time, convert the precursor in the respective oxide[10,20–22]. Our last work in this field was focused on the influence of the polymer on morphology and microstructure[18], confirming the concept of the polymer as a

40 templating agent, but also as variable capable of influencing morphological properties and the size
41 of the final oxide particles. In this work we are proposing a new synthetic route of nanosized MOS,
42 based on the same combination of oxide precursors and polymers (in this case oligomers) as
43 templating agent, exploiting a more simple and fast approach that does not involve an
44 electrospinning step. The ES, before calcination, is indeed replaced by the simple kneading of the
45 precursors in presence of an excess of cyclodextrins.
46 Cyclodextrins (CDs) are a family of cyclic oligosaccharides, composed of α-D-glucopyranose
47 units linked through α -1,4 glycosidic bonds, with a peculiar toroidal structure[23]. CDs are obtained
48 from enzymatic conversion of starch and are renewable and eco-friendly materials. Moreover CDs
49 are biocompatible and biologically degradable[24–26]. The three major and relevant from the
50 industrial point of view representatives of CDs family are the α-CD, β-CD and γ-CD and are
51 composed of 6, 7 and 8 glucopyranose units, respectively.[24,26–28]. The CDs structure, with the
52 presence of a slightly apolar cavity and a hydrophilic external part, determines the ability to
53 establish specific interactions with various types of molecules through the formation of
54 noncovalently bonded complexes, either in the solid phase or in aqueous solution. There are many
55 examples in literature of CDs complexes with many different organic compounds [24,27,29,30] or metal
56 ions[31,32] and cyclodextrins are extensively used in a wide range of applications[26,33].
57 In 2016 [34], Zhang *et al.* employed host-guest inclusion complexes as versatile (the chemical
58 composition of host-guest inclusion complexes can be finely tuned) precursors for obtaining
59 hetero-doped carbon materials.
60 The present work demonstrates the possibility to exploit inclusion complexes of CDs and metal
61 precursors to obtain nanostructured oxide: cyclodextrins plays in this case the role of a sacrificial
62 template. We selected precursors of SnO_2 and ZnO (two MOS traditionally obtained in form of

nanostructures via sol-gel synthesis or, as said, more recently, via electrospinning) because they have been widely investigated in solar cells, photocatalysts and gas sensors [6,19,35,36]: the inclusion complexes were prepared using Zinc Oxide (ZnAc) and Tin (II) - ethylexanoate (SnEx) and exploiting a sustainable and solvent-free approach, completely based on the simple kneading of α-CD, β-CD and γ-CD and precursors in ball mill.

According to the Green Chemistry Principles, published in 1998 by Anatastas *et al.*, chemical processes must be designed in order to "minimize the quantity of final waste and to avoid hazardous or toxic solvents". [37,38] Unfortunately, toxic solvents are present in most of processes: the recovery and reuse are often expensive, and the disposal is a major concern. Even if in much smaller quantities, the process reported in our previous article[18] for obtaining oxides with electrospinning also involves the use of dimethylformamide for the preparation of the polymeric solution to be electrospun.

The use of kneading for the preparation of inclusion complexes with CDs is quite established, permitting to overcome all the limitations related to poorly soluble or insoluble compounds[29,39,40]; in our case permitted to completely avoid the use of solvents and to speed-up the preparation of the MOS precursor.

The complexes after kneading were characterized by thermogravimetric analyses and, subsequentially, thermally treated for the obtaining of the oxide. After the synthesis the so obtained SnO_2 and ZnO nanoparticles were characterized by scanning electronic microscopy (SEM), high-resolution transmission electron microscopy (HR-TEM) and by X-ray diffraction (XRD) and by measuring the BET surface area, evidencing a possible influence of the CDs dimension on the finale oxide.

86 EXPERIMENTAL

87 *Materials*

88 β-CD were provided by Roquette Frères (Lestrem, France) with purity > 95%. α-CD, γ-CD
89 (research grade, purity > 95.0%) were purchased from Cyclolab (Budapest, Hungary) .
90 Cyclodextrins were dried in oven at 75 °C up to constant weight, before use.
91 SnO_2 and ZnO precursors, respectively Tin(II) 2-ethylhexanoate (SnEx, purity grade of 94.4%)
92 and Zinc Acetate (dihydrate, ZnAc), were purchased from Sigma-Aldrich (Steinheim, Germany)
93 and used without further purifications.

94

95 *Ball Mill (BM)*

96 The ball mill used for the kneading step was a Retsch PM200 High Speed Planetary Ball Mill
97 (Haan, Germany), with planetary configuration and Zirconia jars, inner volume 50 mL.

98

99 *Thermogravimetric analyses*

100 Thermogravimetric Analyses (TGA) were performed on a TA Instruments (New Castle, DE, USA)
101 Hi-res Q500 Thermogravimetric Analyzer. TG Analyses parameters are the same for all samples:
102 100 mL/min air-flow, heating rate 10 °C/min, RT to 700 °C. The thermograms were elaborated
103 using TA Instruments Universal Analysis 2000 software and, subsequentially, OriginLab2019b.

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107

108 *Preparation of the samples*

The preparation is the same for all oxides samples and can be divided in 2 parts:

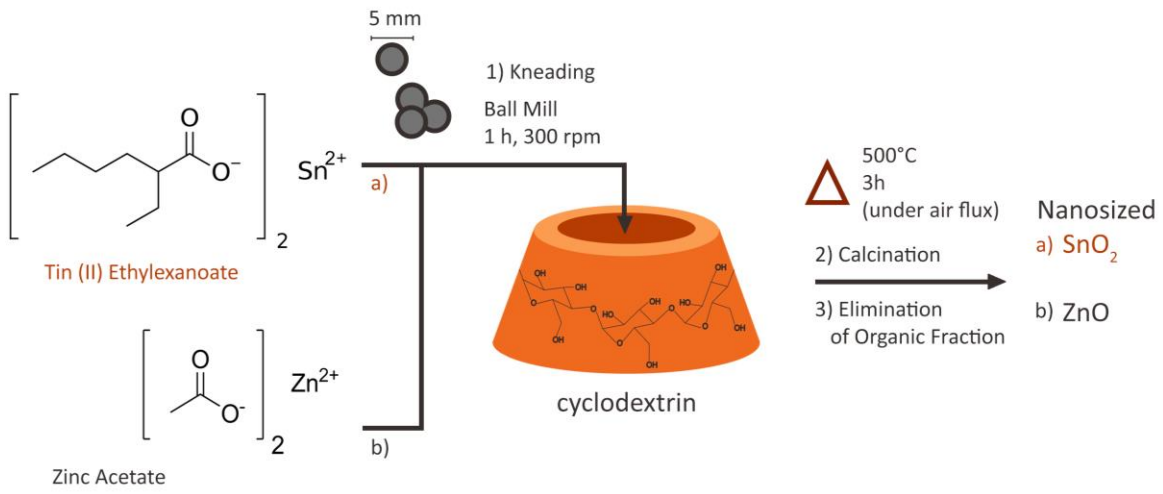
Kneading: an appropriate amount of cyclodextrins (dried powder) is kneaded with the precursor, approximately respecting the molar ratio 2:1, expressing an excess of cyclodextrins.
For Tin(II) 2-ethylhexanoate (viscous liquid): 3 g of α-CD, kneaded with 0.624 g of SnEx; 3 g of β-CD, kneaded with 0.535 g of SnEx; 4 g of γ-CD, kneaded with 0.624 g of SnEx.
For Zinc Acetate (powder): 3 g of α-CD, kneaded with 0.338 g of ZnAc; 3 g of β-CD, kneaded with 0.290 g of ZnAc; 4 g of γ-CD, kneaded with 0.338 g of ZnAc.

The mixtures are kneaded for 1 h at 300 rpm. The size of the balls is 5 mm (declared diameter). Approximately 12 mL (volume, measured with graduated cylinder) of sintered zirconium oxide balls, 5 mm of diameter, in each jar. Quantities of kneaded reactants are optimized for this specific volume of balls and, consequently free volume in the jars.

Calcination/Elimination of Organic Fraction: after calcination all samples were thermally treated to eliminate the cyclodextrin matrix and convert the precursor into the correspondent oxide.
In a typical procedure approximately 8-10 g of mixture cyclodextrin/precursor contained in a Coors combustion boat were inserted in a Lenton (Hope, UK) tubular furnace.
Parameters were optimized via Thermogravimetric Analyses; used conditions were the following: 3h, 500° C, under 100 mL/min air-flow.
A white powder was obtained from all thermal treatments.

Scheme 1, following, shows a schematic representation of the complete procedure.

Further details of the synthesis will be discussed more in deep in the next sections (Results and Discussion).



Scheme 1 - Schematic representation of the proposed kneading-based approach

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X-ray diffraction

X-ray diffraction (XRD) patterns of samples SnO_2 and ZnO obtained after thermal treatment were collected to determine the crystalline phases and the average crystallite sizes by applying the Scherrer's formula on the (xxx) diffraction peak.

XRD) analysis were carried out on a PW3050/60 X'Pert PRO MPD (PANalytical, Malvern, United Kingdom), using as X-ray source a PW3373/10 LFF with Cu Anode, $\lambda = 0.541$ Å.

BET

Gas-volumetric analysis Nitrogen adsorption–desorption isotherms were measured using a Micromeritics ASAP2010 volumetric sorption analyzer (Norcross, GA, USA). Before

149 measurements, the samples were outgassed at 100 °C under vacuum (10 mm Hg) for 15 hours (for
150 removing water and eventual adsorbates). The specific surface areas were determined through the
151 Brunauer-Emmett-Teller (BET) method to the adsorption/desorption isotherms of N_2 at 77 K.
152
153 *SEM*
154 Morphological characterization of the samples was performed by scanning electron microscopy
155 (SEM), using a Tescan VEGA 3 SEM (Brno, Czech Republic) working with secondary electrons
156 and 10keV accelerating voltage. The samples were analyzed without any previous metal coating.
157
158 *TEM*
159 High-resolution transmission electron microscopy (HR-TEM) was utilized to achieve further
160 morphological and structural information: the instrument is a Jeol (Akishima, Tokyo, Japan) JEM
161 3010 UHR (300 kV, LaB6 filament). The synthesized samples were deposited on a Cu grid, coated
162 with a porous carbon film. All digital micrographs were acquired by an Ul-traSscan 1000 camera,
163 and the images were processed by Gatan digital micro-graph (Pleasanton, CA, US) .
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169 RESULTS AND DISCUSSION

170 The starting point for this project is the idea of using a polymer as a sacrificial template to obtain
171 very small oxide particles for specific applications. The focus is therefore on the final resulting

oxide but, as we recently demonstrated [18], the influence of the polymer on the precursor conversion is dramatic. The choice of the templating polymer, consequentially, is of primary importance. Our choice fell on cyclodextrins for different reasons: CDs are a widely studied oligomer [25], with an extensive literature that supports many of our claims, CDs are a renewable because obtained from enzymatic conversion of starch [24,25]. Thus, CDs are renewable, eco-friendly materials and, last but not least, cheap. In Figure 1, following, are reported a simplified chemical structure of a α, β and γ CDs and the respective dimensions of the CDs employed in the present work.

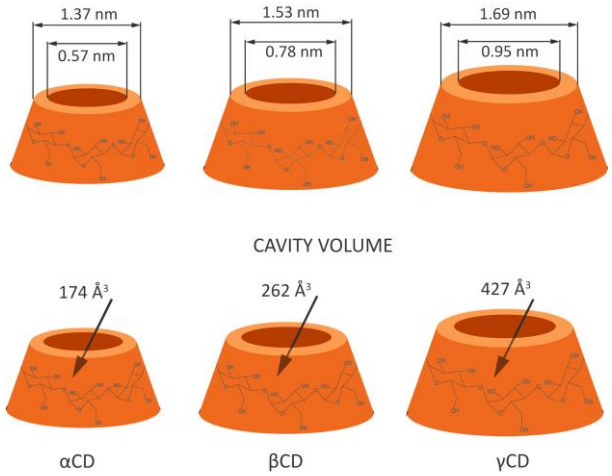


Figure 1 - Simplified structure and dimensions of α, β and γ cyclodextrins

α, β and γ cyclodextrins exhibit a different size and a different cavity volume (Figure 1, details). The principle behind exploiting CDs as a sacrificial "container" is also associated the relatively high degradation temperature of the pristine CDs, that is roughly around 300°C for α, β and γ cyclodextrins: this is a crucial parameters, because the polymer "matrix", in this case the oligomer, needs to be completely removed in an efficient way, but still needs to protect e to assist in a synergic way the formation of the oxide. In order to obtain the SnO_2 and ZnO, it is necessary to achieve the complete volatilization of the polymer and the degradation organic precursor [19]. An

incomplete elimination of the organic fraction will lead to a grey/black powder, with an amorphous carbon residue. At the same time, a high temperature can affect the final size of the oxide, which could favor crystal growth during calcination rather than nucleation, leading to bigger particle and lower surface area. In Table 1, following, are reported all the synthetic information and the BET surface area, [m^2/g]. A careful correlation of the results shown in Table 1 with the thermal measurements shown in Figure 2 and Figure 3 (and with data already present in literature), allows us to make some assumptions.

Table 1 – Oxides (α, β and γ SnO_2 and α, β and γ ZnO), relative preparative conditions (kneading step and subsequential thermal treatment) and BET Surface Area (m^2/g)

OXIDE		Precursor	Kneading	Thermal Treatment	BET Surface Area [m^2/g]
SnO_2	α-SnO_2	Tin (II) ethylexanoate	1 h 300 rpm 5,0 mm Ø balls 10 min inversion time	3 h 500°C ramp 10 °C/min	44,2
	β-SnO_2				47,1
	γ-SnO_2				50,4
ZnO	α-ZnO	Zinc Acetate	1 h 300 rpm 5,0 mm Ø balls 10 min inversion time	3 h 500°C ramp 10 °C/min	12,0
	β-ZnO				10,5
	γ-ZnO				17,5

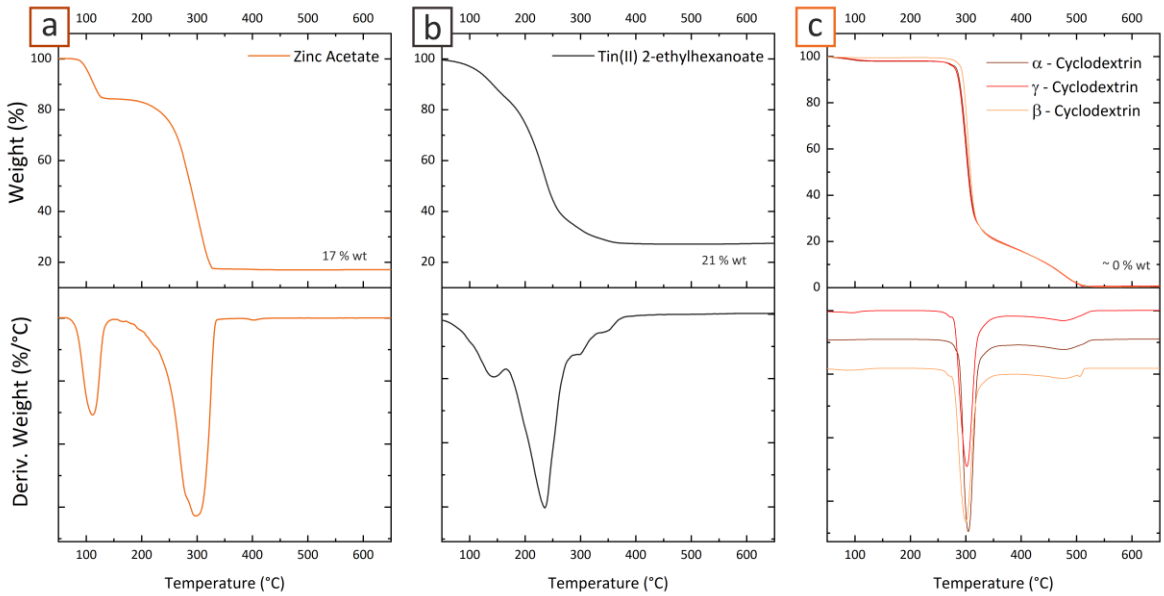
As shown in Table 1, the preparative conditions are the same for all samples: nevertheless, outcomes are quite different. The BET Surface area for what concerns the SnO_2 is comprised between ≈ 44 and 50 m^2/g, for all CDs template, a quite interesting result, comparable with the results reported in the literature with oxides and similar treatments REF. It is necessary to underline, however, that these very interesting results were obtained through an objectively very simple preparation, without complex procedures and, even more noteworthy, without any solvent

206 in any step. However, the same reasoning cannot be made with regard to ZnO. The oxide obtained
207 has a much lower surface area, indeed. SnO_2 and ZnO are certainly two completely different oxides
208 but the dramatic difference in the final result is clear. Still, the presence of a trend in both oxides
209 from different precursors is evident: the surface area appears to be (with the sole exception of β-
210 ZnO, Table 1 for reference) inversely proportional to the size of the cyclodextrin cavity. It is worth
211 to say that the formation of an inclusion complex is not the only possible way of CDs to form
212 complexes: stable interactions are sometimes established between a guest molecule and the
213 external part of CDs. Indeed, hydroxy group on the outer surface of cyclodextrins can lead to the
214 formation of hydrogen bonds and, consequentially, to water-soluble complexes, in a similar way
215 to what is seen with non-cyclic oligo or polysaccharides [27,41]. These supramolecular assemblies
216 (there are no covalent bonds) are called *non-inclusion* complexes. They can, eventually, protect
217 guest molecules from the environment and achieve anyway an efficient increase of solubility. In
218 literature many examples of non-inclusion compounds are reported [42–45]. Among the others there
219 is, of course, the size compatibility between host and guest molecules. The size of CD has to be
220 large enough to permit the guest entrance but if the guest is too small if compared to the cavity,
221 CD-guest interactions will be very weak, and the dissociated form will prevail on the associated
222 one. The same applies for the opposite situation: a molecule larger than the cavity will enter
223 partially or will arrange outside the cavity. An example in literature is, for example, the
224 naphthalimide, where the apolar chain fit preferentially in a smaller α-cyclodextrin cavity, wherein
225 the aromatic moiety of the same molecule will arrange inside a β-cyclodextrin [46].
226 It is therefore possible to hypothesize that there is not the real formation of a 1: 1 complex, but
227 rather the formation of "clusters". Given the interesting results these clusters are necessarily of
228 small size; thus, it is possible to assume that in any case the ion or the precursor are, statistically,

229 partially or completely incorporated by the cyclodextrins and this is more probable with the γCD,

230 whereas the cavity is larger. This hypothesis can also be supported by a possible interpretation of

231 the thermogravimetric analyses, Figure 2 and Figure 3, following.



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233 **Figure 2 - Comparison of thermo-gravimetric analysis (TGA) and derivative TGA (DTGA) of the different**
234 **component of the precursor mixture in air, from RT to 700 °C, 10 °C/min. Respectively a) Zinc Acetate b) Tin**
235 **(II) ethylexanoate c) α, β and γ Cyclodextrins**

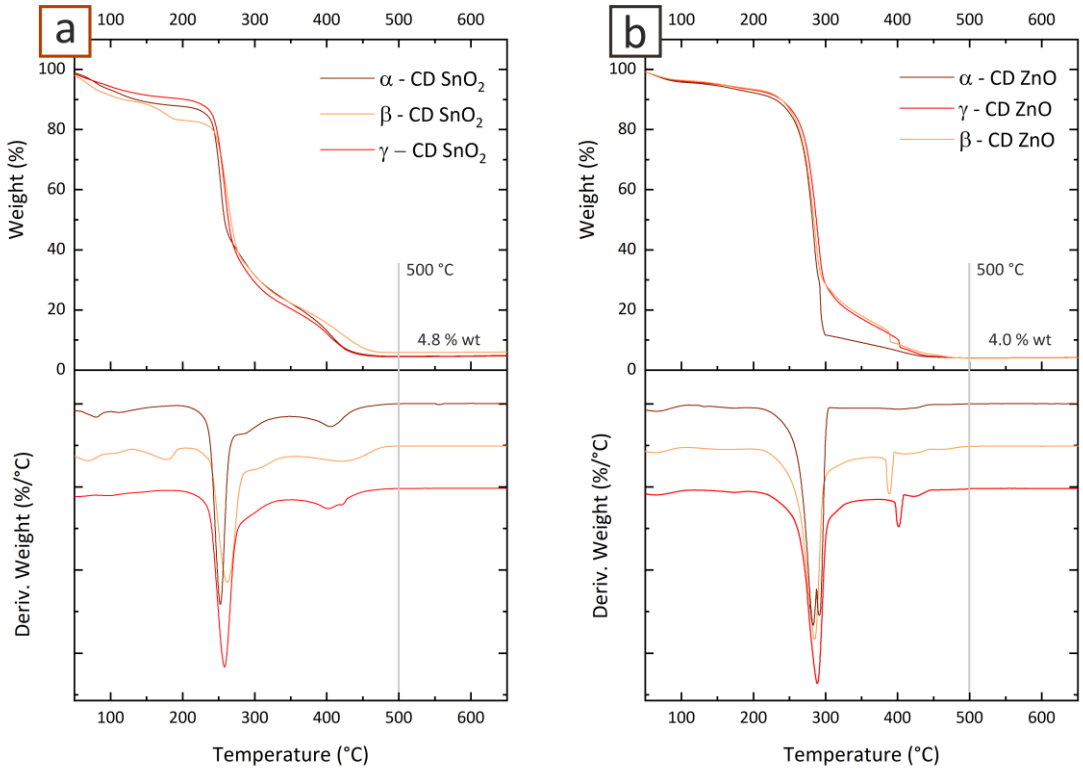

Figure 3 - Comparison of thermo-gravimetric analysis (TGA) and derivative TGA (DTGA) ir, from RT to 700 °C, 10 °C/min. a) α, β and γ SnO_2 from Tin (II) ethylexanoate/CDs and b) α, β and γ ZnO from Zinc Acetate/CDs

In Figure 2, the thermo-gravimetric analyses and derivative TGA of the different component of the precursor mixture in air, from RT to 700 °C, are reported. The degradation of ZnAc, inset a) Figure 2, shows a thermal degradation that proceeds in two different steps: the first one at 100°C reasonably related to the water and the second one, that starts before 300°C and that leads to a residue of 17%, can be related to the decomposition of ZnAc itself, that is only partially converted into ZnO (ZnAc is reported to sublimate at 234 °C[47]). Assuming a total conversion of the precursor into ZnO the residual should amount to approximately 37% wt. A similar situation is shown with the Tin (II) ethylexanoate, inset b) Figure 2, where the residue from TG is around 21%: also in this case the expected quantity of residue, with a complete conversion of the precursor in SnO_2, is 37%.

250 In both precursors, there is a competition between degradation and oxidation, indeed. A different
251 situation is shown in Figure 2, inset c), concerning CDs. The degradation can be divided in three
252 stages[48]: the first one, below 100°C, due to loss of absorbed water and water of crystallization (in
253 this case, since CDs were dried for at least 24h, the weight loss is barely detectable), the second,
254 that develops in a temperature range that start at roughly 250 °C, which is associated with a weight
255 loss of 70-80%, with the formation of a char residue and the third, at T > 300 °C, that leads to
256 complete oxidation (combustion) of the residue.
257 The final residue, after the third stage, is ≈ 0% for all cyclodextrins. Cyclodextrins alone, therefore,
258 in an oxidizing atmosphere, do not leave any residue.
259 Consequentially, looking at the thermogram reported in Figure 3, showing a residue around 4.8 %
260 for SnO2 and 4.0 % for ZnO, it is possible to state that the simultaneous presence of CDs and
261 precursor leads to the formation of an oxide and that the cyclodextrins are completely eliminated
262 from the mixture above 450 ° C. In both thermograms, inset a) and b) Figure 3, most of the weight
263 loss profile is related to the volatilization of the cyclodextrin matrix, and this is consistent with
264 what it was possible to hypothesize considering the initial composition of the mixture after
265 kneading. What is necessary to highlight is the amount of residual oxide, because it could confirm
266 a protective effect of the cyclodextrins: the theoretical residue in oxide, assuming a total
267 conversion of the precursor present in the post-kneading mixture is 4.5 % for ZnO and 5.6 % for
268 SnO_2, respectively. Thus, results are remarkably close to the 4.0 % and 4.8 % reported before. The
269 yield is low, but we must consider that the precursor/CDs kneaded mixture contains approximately
270 15% wt. of precursor: tin (II) 2-ethylhexanoate and zinc acetate, if heated in the same conditions,
271 volatilize, leaving a considerably smaller amount of residue, while in this case the precursor is
272 almost completely converted into oxide.

Cyclodextrins, therefore, do not only play a role of simple support but rather protect and assist the formation of oxide (preventing the volatilization of the precursor), influencing both its yield and final size.

However, it is necessary to make further considerations, about the possible reasons why the same interesting results, concerning the BET surface area (and consequentially particle size) were not obtained as for SnO_2 with ZnO. In Figure 2 it is evident that cyclodextrins have their principal weight loss at a temperature comparable to that of zinc acetate, while it is about 50 °C higher than that of tin (II) 2-ethylhexanoate: given the results previously commented and assuming therefore that there is a protective effect, this is effective only if the “shield” molecule does not degrade before the host molecule.

Moreover, a less effective protective effect can also be hypothesized from an analysis of the TG curves reported in inset b) of Figure 3: in the area around 400 degrees, where in presence of oxygen presumably occurs the oxidation/combustion of the cyclodextrins, it is possible to notice an anomalous behavior (very evident in the peaks of the first derivative). These small weight losses can be related to volatiles that are quickly released as soon as the protective "cage" is thermally oxidized. Given the tendency of ZnAc to sublimate, reported in the literature, it can be hypothesized that part of the precursor is actually not converted but rather simply "blocked" and subsequently lost during the heating.

Another plausible reason in the different superficial area from a comparison of the two different precursors can be related to the fact that in the case of the SnO_2, the kneading phase is carried out with a liquid precursor, tin (II) 2-ethylhexanoate, instead of a powder such as in the case of the Zinc Acetate: the liquid form of the precursor leads to a much more effective grinding / mixing,

leading to the obtainment of a sort of "paste". From a practical point of view, the kneading phase therefore seems to have a significant influence on the final result.

We also characterized the final oxides from the morphological point of view by scanning electron microscopy, results are shown below (Figure 4):

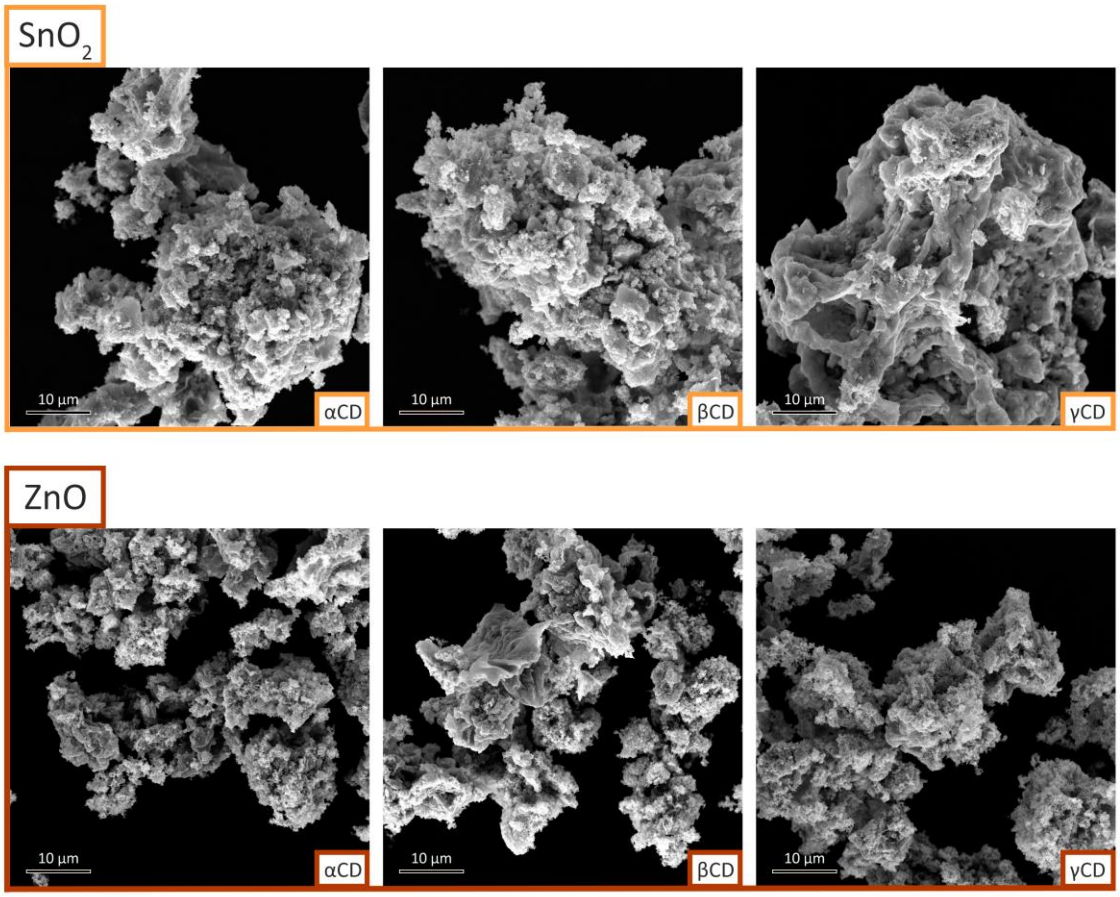

Figure 4 SEM images of the oxide obtained from different precursors and CDs. Instrumental magnification 5kx, 10keV

The suitable temperatures for calcining the mixture after the kneading step were chosen on the results obtained by TG analyses, considering the temperatures at which the weight losses are concluded: the same temperature, 500 °C was, used for the calcination of all kneaded mixtures,

leading to a white and uniform oxide residue. As shown in Figure 4, there are no particular differences that emerge from the SEM comparison of the samples, even if obtained from different mixtures of oxides and oligomers. Higher magnification are reported in Supporting Informations.

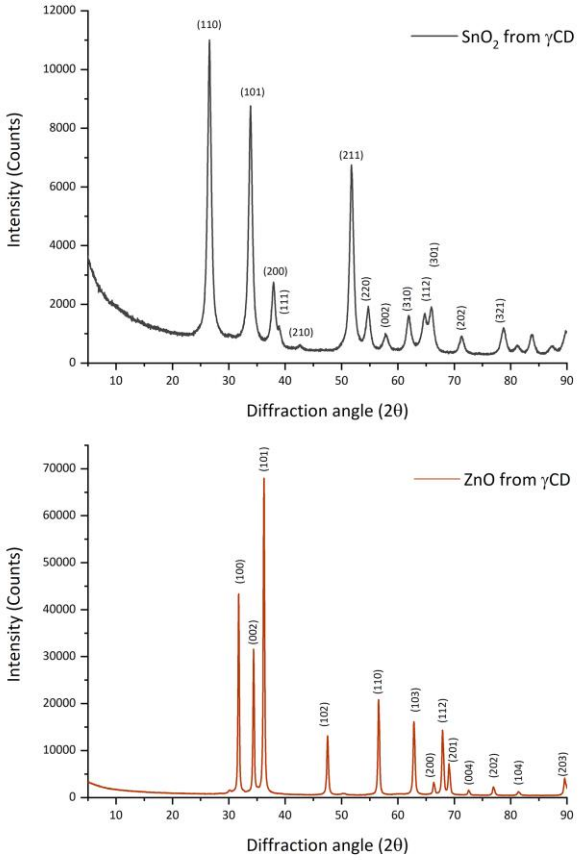

Figure 5 XRD patterns of SnO_2 and ZnO, from precursot/γCD mixtures.

The XRD confirms that the samples are constituted by crystalline cassiterite (SnO_2 in the tetragonal crystal phase, JCPDS file number 00-001-0625). The calculated size (D, via Debye-Sherrer equation) is …..

TEM

CONCLUSIONS

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ABBREVIATIONS

αCD, alpha-cyclodextrin; βCD, beta-cyclodextrin; γCD, gamma-cyclodextrin; BM, ball-mill; SnEx, Tin(II) 2-ethylhexanoate; ZnAc, Zinc Acetate;

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TOC/GRAPHIC ABSTRACT

SYNOPSIS