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COMMUNICATION

Solid *vs*. hollow oxide spheres obtained by hydrothermal carbonization of various types of carbohydrates

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Saccharide derived, self-templated carbonaceous spheres with embedded Zn (and Co) were obtained by a versatile one-pot hydrothermal synthesis and proved to be multipurpose precursors for full solid or hollow oxide spheres. Saccharide/Zn^{2+} ratios and saccharide type affects the morphology (size, shell thickness, surface roughness) of the oxide spheres.

The development of environmentally acceptable chemical protocols implies *inter alia* a reassessment of natural compounds. Saccharides, possessing versatile properties and unquestionable green characteristics may be considered as one of green chemistry "crown jewels", whose potential in material science is far from fully utilized yet.[1] Current interest is focused on the renaissance of traditional processes and materials that, benefiting from scientific advances could increase their applicative values. An illustrative example is the hydrothermal carbonization (HTC) of biomass. Reported by Bergius,[2] is rediscovered one hundred years later as an alternative for modern carbon-based materials *design*.[3] Wang *et al*. described first the synthesis of carbon rich microspheres through HTC of sucrose.[4] Subsequently, the range of the raw materials was extended from mono- to polysaccharides, either hexose or pentose sugars,[5-7] even complex biomass[8]. Carbonaceous spheres have proved to be efficient carbon sources and templates for metal-carbon[9,10] or metal oxide-carbon composites,[11] but their most extensive use is by far as sacrificial templates for the synthesis of metal oxides hollow structures.[12,13] Generally, hollow oxides synthesis implies three steps: template synthesis (*via* HTC of the saccharide), metal incorporation (taking advantage of outer surface oxygen functionalities) and template thermal removal.[12,13] The combination of template synthesis and metal encapsulation into one step (scarcely investigated) upgrades the method by saving time and labor. Fe_2O_3, Co_3O_4, NiO, MgO, CuO, ZnO hollow spheres[14,15] were obtained using glucose:metal molar ratios (R) from 15:1 to 1:1, CuO with R ranging between 375:1 and 37.5:1,[16] while WO_3[17] at R=30:1, and In_2O_3 hollow spheres[18] using R (sucrose:indium) of 6:1 and 60:1.

Herein, we reveal three novel facets of the HTC methodology: (*i*) the extension of the procedure to the synthesis of solid spheres (exploiting the high loading of the metal cation on/into the template) (*ii*) the effect of the saccharide used as template over size and surface features of the spherical metal oxide structures, and (*iii*) the synthesis of multi-oxide spheres (using the incorporation of cobalt as additional metal, besides zinc).

A one-pot hydrothermal process was used for the fabrication of self-templated carbonaceous spheres with embedded zinc. Thermal processing led to the evolving of the sacrificial template and formation of ZnO spheres, either hollow or full solid. The switch from hollow to solid oxide sphere morphology is dictated by the raw materials molar ratio (Fig. 1): the change hollow↔full solid oxide spheres is achieved at $R < 2$ irrespective of the carbohydrate. Hollow spheres form in the range $2 < R \leq 20$; an increase of the zinc amount in this domain does not increase the size of the spherical shell diameter, but develops a denser and thicker shell since a greater amount of metal oxide entails a closer packing of the crystallites. Full spheres, with diameters similar to the hollow ones, form for $R < 2$. An additional metal incorporation leads to diverse multi-oxide spherical structures ruled by the used deposition technique and heating treatment. The HTC process yield undergoes a decreasing trend (down to ~ 60%) with the increase of R.

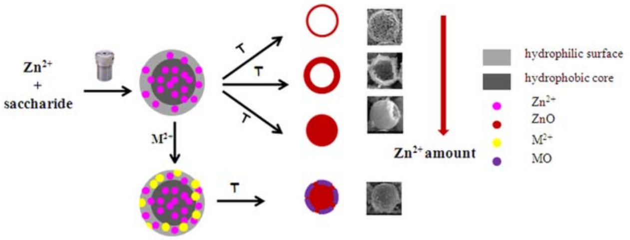

Fig. 1. Schematic illustration of the approach to ZnO-based spherical structures

The key parameter of the synthesis is the presence of metal cations during the HTC of the saccharides, permitting their

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efficient embedding within the template and therefore a high metal cation loading. If the deposition is performed *post* carbonaceous spheres synthesis, the location of the cations is restricted by and to the spheres' surface, although the incorporation can be aided, *i.e.* by ultrasonication.[11,19] The metal concentration does not affect the mode value of the spheres diameter, which is related only to the parent carbohydrate, while the distribution of both precursor and ZnO sphere diameters widens with zinc content increase (lower R, Fig. 2).

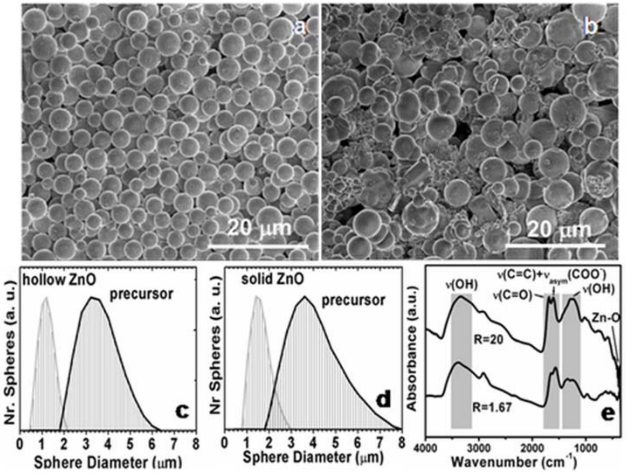


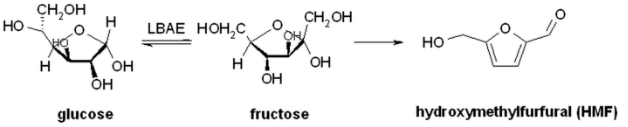
Fig. 2. SEM micrographs of sucrose-derived precursors: (a) R=20; (b) R=1.67; the size distribution of precursors and their corresponding oxides: (c) R=20 and (d) R=1.67; (e) FTIR spectra of the two precursors.

An increased quantity of zinc source lefts its mark on the density of the surface functional groups (Fig. 2e). As a result of hydroxyl groups involvement in different linkages with zinc ions (coordination, supramolecular and/or electrostatic ones),[20] the ν(OH) vibration from ~ 3440 cm^{-1} assigned to water molecules and/or hydroxyl groups decreases and turns slightly narrower due to a certain ceasing of the hydrogen bonds, while the bands positioned in the range 1500-1100 cm^{-1} are better structured.[21] The retention even at high Zn^{2+} concentration, of the surface functional groups characteristic to the pristine carbonaceous template (Fig. S1†) makes the surface available for further functionalizations as additional incorporation of metal cations (*vide infra*).

At R < 2 without regard to the used saccharide, the obtained oxide spheres are full solid (Fig. 3 and S2†). To the best of our knowledge, there have been no reports on such templating behavior of carbonaceous derived spheres, proving that our approach permits the homogeneous embedding of a large amount of zinc into the carbonaceous precursor spheres (Fig. 2) during the HTC process.

The surface of the solid oxide spheres is smooth, compact, except for pores generated from ousting of gases evolved from carbonaceous material, typically much smaller than oxide grain sizes. Mechanically broken solid spheres show an outer shell with smaller particle size, and a polycrystalline core with significantly bigger grains and pores (Fig. 3). The full ZnO spheres derived from monosaccharides have smaller sphere diameters (about 3 and 4 times, Fig. 3q) in comparison with those from di- and polysaccharides. Fructose is the precursor carbohydrate that yields the smallest solid spheres and a narrow distribution of sphere diameters. Sucrose and starch led to wider distributions and higher mode values for all R values.

Concerning the hollow spheres synthesis, the method has two strong points: (*i*) permits the formation of ZnO hollow structures at high molar R (20) where other methods failed,[15] and (*ii*) the surface features of the obtained hollow spheres are dependent on the used carbohydrate (Fig. 3). Fructose and sucrose derived oxide shells appear thin (20 nm), uniform, with porous filigree-like patterned walls; the oxides derived from glucose and starch have thicker walls (100-200 nm) and rough, rocky-like surfaces, disrupted by intergranular steps and gaps. Such malleability could be advantageous for surface related applications. This versatility and the yield downtrend related to the precursor saccharide already mentioned is correlated with the existence of different Zn^{2+}-OH linkages in each carbohydrate. We advance the following explanation based on hydroxymethylfurfural (HMF) developing during the HTC process. HMF is considered as the main reactive intermediate; once formed it is subsequently *in situ* condensed/polymerized, forming carbon-based materials. HMF is directly obtained only from fructose *via* intramolecular dehydration (Scheme 1).[8,22] When the starting carbohydrate is glucose, an initial isomerisation reaction into fructose takes places according to a Lobry de Bruyn-Alberda van Ekenstein (LBAE) rearrangement.[23] In our case, the presence of zinc linked to the carbohydrate hinders both isomerisation and carbonization steps (the last arises from cross-linking induced by intermolecular dehydration of the intermediaries formed in the earlier steps). Consequently, several effects have to be mentioned. First, in the specific case of glucose and starch, the formation of zinc supramolecular assemblies (clusters) with different nuclearities may occur during the prolonged initial stages of the synthesis, in a reaction medium in which the saccharides act as flocculants.[24] The features of the corresponding hollow spheres sustain the affirmation. Secondly, with the increase of zinc content, the HTC process needs longer times. This is consistent with the SEM images of the precursors (Fig. 2a, b): while for low zinc concentration, the spheres have relatively homogeneous sizes and nearly perfect spherical shapes, at higher zinc concentration, numerous small particles coexist with large spherical structures and clusters composed from smaller spheres. The diameters of the hollow ZnO spheres vary in a similar manner to solid ones (Fig. 3r). The dual distribution in glucose-derived hollow spheres can be explained by its delayed dehydration (Scheme 1).



Scheme 1. Glucose to fructose isomerisation and subsequent dehydration to HMF.

The XRD analysis (Fig. S3†) confirmed that spheres are composed of crystalline ZnO, with crystallite sizes related to the used saccharide and zinc amount (higher values for ZnO derived from glucose and starch composites and higher metal concentration). A good crystal quality of the ZnO structures is also observed by Raman spectroscopy (Fig. S4†). The solid spheres present a strong blue emission (rarely encountered for ZnO),[16,25] a promising characteristic for biological fluorescence labeling applications (Fig. S5†).

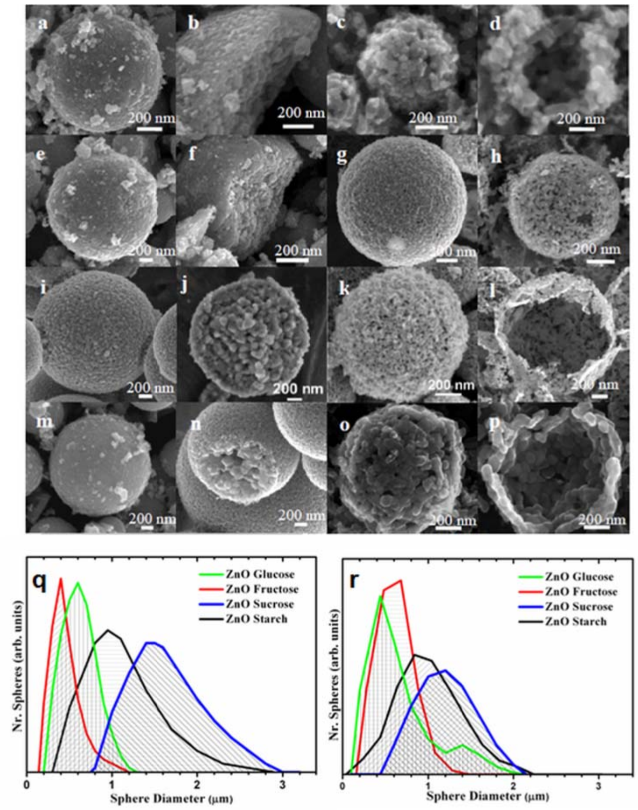


Fig. 3. SEM micrographs of (a-b, e-f, i-j, m-n) full (R=1.67, 600°C/1h) and (c-d, g-h, k-l, o-p) hollow (R=20, 600°C/1h) ZnO spheres, whole and mechanically broken: (a-d) glucose; (e-h) fructose; (i-l) sucrose; (m-p) starch; diameter distribution for (q) full and (r) hollow spheres.

We explored the formation of double oxide spheres *via* incorporation of cobalt cations in the Zn-loaded carbonaceous spheres (Fig. 4). SEM, elemental mapping, TEM and EDX measurements demonstrated the presence of cobalt in the oxide spheres formed after calcination (Fig. S6†, S7†). Furthermore, core-shell double oxide spheres (Fig. 4d-f, Fig. S6†), with a Zn-rich core and a Co-rich shell, separated by a void space, were obtained by decreasing the zinc content. As a general rule, provided the same calcination procedure is used, the internal void space in the core-shell spheres shrinkages with increasing zinc concentration, till full solid spheres (Fig. 4a-c) are obtained.

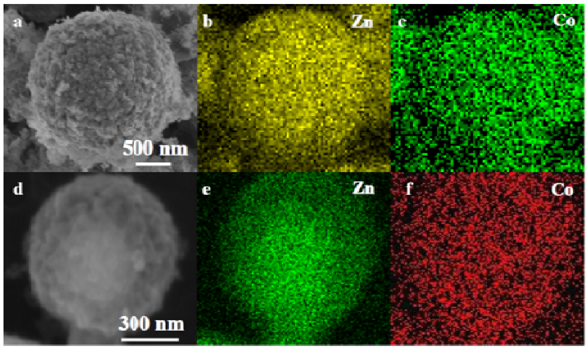


Fig. 4. SEM micrographs and elemental mapping of zinc-cobalt double-oxide spheres. (a-c) full solid (R=1.67, 500°C/1h, starch) and (d-f) core-shell (R=5, 500°C/1h, starch).

Conclusions

We have demonstrated here that the hydrothermal all-in-one synthesis which starts from a zinc salt and mono, di- and polysaccharide may be developed as a general synthetic convenient methodology towards tunable hollow and full ZnO spheres. It was generally considered until now that the type of carbohydrate does not influence the final characteristics of oxide structures, our results prove that the surface features (mainly for hollow spheres), the size of ZnO crystallites and the spheres diameter are related to the parent carbohydrate template. The adopted morphology depends on the used zinc concentration. The straightforwardness of the approach, the ease of adjustment of the structure type and size, and the accessibility for further functionalization represent decisive factors for transferring the procedure to other oxide systems. The synthesis of double-oxide spheres was demonstrated by the incorporation of an additional metal. A complete knowledge of the synthetic route capability needs a "chess table" type investigation in terms of carbohydrate and metal cation in oxide systems, but until then a paradigm have been broken: saccharide-derived spheres may work as template for obtaining full solid and not only hollow spherical structures. The results are a good example of how natural compounds can induce versatility in materials synthesis.

Acknowledgements

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Solid *vs.* hollow oxide spheres obtained by hydrothermal carbonization of various types of carbohydrates

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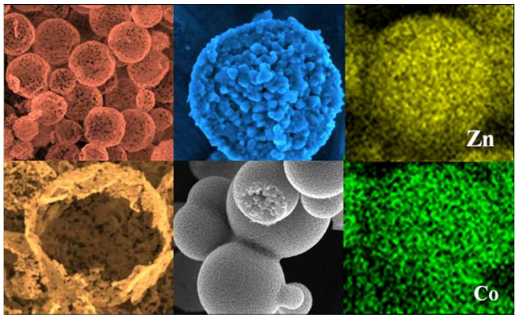

The zinc embedded self-templated saccharide derived carbonaceous spheres proved to be multipurpose precursors for hollow, solid and double oxide spheres.