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A Generalized Synthesis of Metal Oxide Hollow Spheres Using a Hydrothermal Approach

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Hollow spheres of crystalline metal oxides were synthesized in a simple one-pot synthesis via a hydrothermal approach. Various metal salts were dissolved together with carbohydrates in water, and the mixtures were heated to 180 °C in an autoclave. During the hydrothermal treatment, carbon spheres are formed with metal ions incorporated into their hydrophilic shell. The removal of carbon via calcination yields hollow metal oxide spheres. Using this process, we can produce a wide range of metal oxide hollow spheres that are not accessible via sol−gel chemistry. In this paper, we report the synthesis of Fe_2O_3, NiO, Co_3O_4, CeO_2, MgO, and CuO hollow spheres that are composed of nanoparticles. The surface area and thickness of the shell can be varied or controlled by the carbohydrate:metal salt concentration.

Introduction

Hollow spheres of metal oxides have recently attracted a great deal of attention because of their wide variety of applications, including catalysis, the delivery and controlled release of drugs, as building blocks in the fabrication of photonic band gap crystals, microcapsule reactors, chemical sensors, and so on. The most-applied method for the synthesis of hollow micro- or nanospheres is by far the templating of larger colloidal particles. The templates can be of different composition, for example, silica,[1] polymer,[2−4] or carbon particles[5] (hard templates), but also vesicles,[6−8] emulsions,[9−11] micelles[12,13] (soft templates), and even gas bubbles[14] have been used. The coating of the particles can be achieved by surface precipitation of suitable inorganic precursors or in a more controlled manner by layer-by-layer self-assembly of polyelectrolyte and inorganic nanoparticles.[15,16] An interesting sacrificial core is represented by monodisperse carbon particles, which are generated by the hydrothermal treatment of aqueous solutions of glucose and polysaccharides.[17,18] These sacrificial cores inherit functional groups and have reactive surfaces, which facilitate the precipitation of metal precursors and nanoparticles, as was shown by Li and co-workers for different materials, for example, TiO_2,[19] Ga_2O_3,[20] WO_3,[21] and noble-metal nanoparticles,[22] which could be fabricated as hollow spheres.

In the present contribution, we show that this promising approach can be even more simplified and generalized. Instead of fabrication by a multistep process that involves the formation of the carbon sphere using hydrothermal treatment, isolation and purification of the carbon spheres, coating of the sacrificial cores with the metal oxide precursors, and subsequent removal of the carbon cores via calcinations, we add metal salts directly to the carbohydrate solutions in water, followed by a hydrothermal treatment. Upon calcination, hollow spheres of various metal oxides, such as Fe_2O_3, Ni_2O_3, Co_3O_4, CeO_2, MgO, and CuO, were obtained. The hollow spheres exhibit diameters from one to several micrometers and consist of nanocrystals of the respective metal oxides.

Experimental Section

D-Glucose monohydrate was purchased from ABCR GmbH (Karlsruhe, Germany). Ammonium iron(II) sulfate hexahydrate

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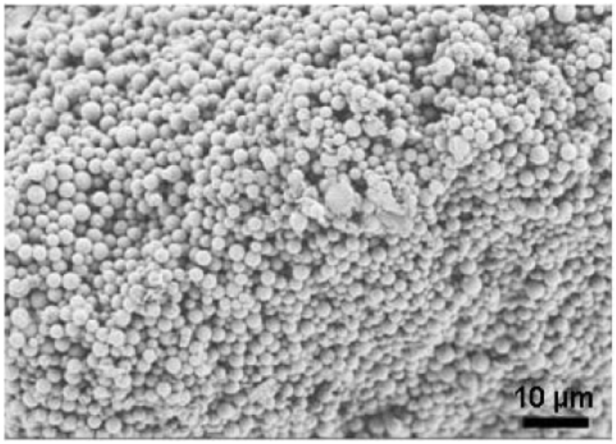


Figure 1. SEM image of carbon spheres obtained from the hydrothermal treatment of glucose.

($(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$) and ammonium nickel sulfate hexahydrate ($(NH_4)_2Ni(SO_4)_2 \cdot 6H_2O$) were obtained from Aldrich (Steinheim, Germany). Cerous nitrate hexahydrate ($Ce(NO_3)_3 \cdot 6H_2O$), cobalt(II) sulfate heptahydrate ($CoSO_4 \cdot 7H_2O$), and magnesium chloride hexahydrate ($MgCl \cdot 6H_2O$) were purchased from Fluka (Deisenhofen, Germany). Copper(II) sulfate pentahydrate ($CuSO_4$ $5H_2O$) was obtained from Strem Chemicals Inc. (Newburyport, MA).

Glucose (3.75 g, 18.9 mmol) was dissolved in 20 mL of distilled water. In a standard experiment, 3.75 mmol water-soluble metal precursors were dissolved in 10 mL of distilled water (the carbohydrate:metal molar ratio was 5:1, thus defining the later shell thickness of the hollow spheres). For Fe, $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ was used as the metal precursor; the amount used during the hydrothermal carbonization was varied from 1.25 to 11.25 mmol (with the carbohydrate:metal molar ratio varied from 15:1 to 1.7:1).

The two solutions were mixed immediately before the experiment and placed in a 45 mL capacity Teflon-lined stainless steel autoclave, which was heated in an oven to 180 °C for 24 h. The products were filtered off; they were washed several times, first with distilled water and then ethanol, and finally dried in a vacuum oven at 60 °C for 5 h. After synthesis, the metal oxide−carbon composites were calcined in air at 550 °C (heating rate of 4 °C/min) for 4 h to remove the carbon core, leading to hollow metal oxide particles. For the formation of hollow spheres composed of copper oxide, sucrose is favorably used as a carbohydrate instead of glucose.

The products were characterized by X-ray diffraction (XRD) in reflection mode (Cu Kα radiation) on a Bruker D8 diffractometer. The particle size and morphology was visualized using a Gemini scanning electronic microscope (SEM) and an Omega 912 transmission electron microscope (TEM) (Carl Zeiss, Oberkochen, Germany). Nitrogen adsorption and desorption isotherms were measured at 77 K with a Micromeritics Tristar 3000 system. For the determination of the surface area, we used the BET method.

Results and Discussion

In Figure 1, a typical SEM micrograph of the carbon spheres produced via the hydrothermal treatment of glucose/water solutions without additives are shown. The experimental parameters used by us result in carbon spheres with diameters of around one micrometer, assuming that impurities are carefully avoided.

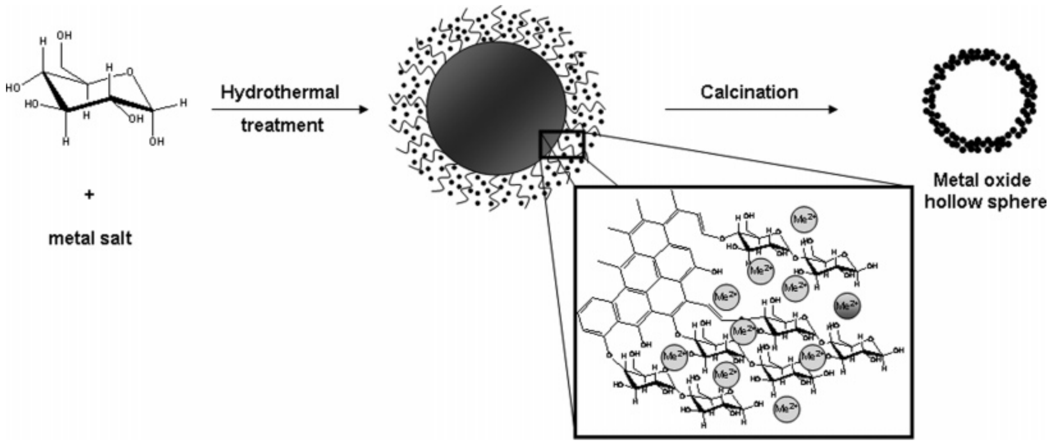
A simplified reaction mechanism of the formation of the carbon spheres involves the dehydration of the carbohydrate in the first step and subsequent carbonization of the so-formed organic compounds in the second step. The surface of the spheres is hydrophilic and has a distribution of OH and C═O groups, which are formed from non- or just partially dehydrated carbohydrates. Elemental analysis reveals a carbon content of around 92%; the remaining mass can be attributed to the oxygen and hydrogen atoms in the hydrophilic shell.

In all experiments described here, the addition of metal salts to the carbohydrate solutions yields an increase in the diameter of the carbon spheres, indicating either a catalysis of the hydrothermal carbonization of carbohydrates or an influence on the colloidal stability of the primary particles formed under hydrothermal conditions. We assume that, during the reaction, metal ions and their resulting nanoparticles are predominantly positioned near the hydrophilic shell of the carbon particles (Scheme 1).

Upon filtration of the solid content and calcination, we obtained hollow spheres of the corresponding metal oxides. SEM micrographs of the spheres before and after calcination reveal a considerable shrinkage (from approximately 5 μm to 1 μm in diameter) of the structures during heat treatment, showing a transition from loosely adsorbed metal ions to a dense metal oxide network in the hollow spheres.

Using this approach, a variety of metal oxide hollow spheres with comparable size can be produced, provided that

Scheme 1. Schematic Illustration of the Synthesis of Metal Oxide Hollow Spheres from Hydrothermally Treated Carbohydrate/Metal Salt Mixtures



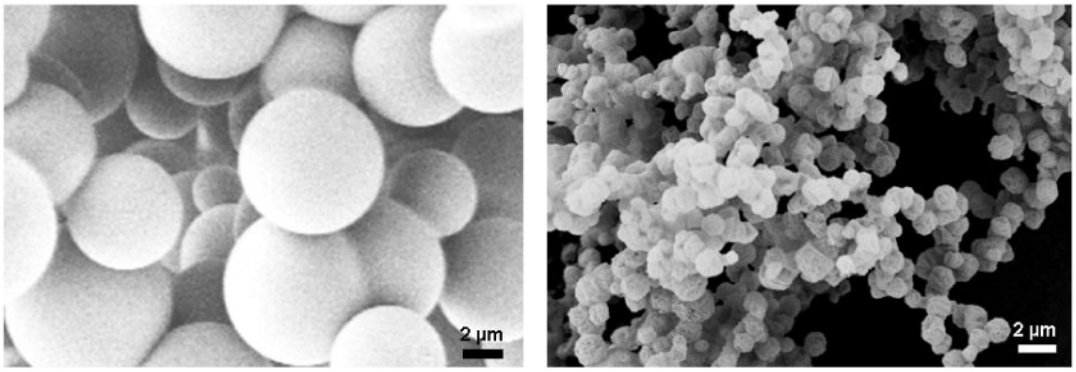


Figure 2. SEM images of carbon spheres produced via hydrothermal synthesis with added iron salts ($(NH_4)_2Fe(SO_4)_2{\cdot}6H_2O$) and a low magnification picture of the iron oxide hollow spheres obtained after calcinations, indicating their homogeneity.

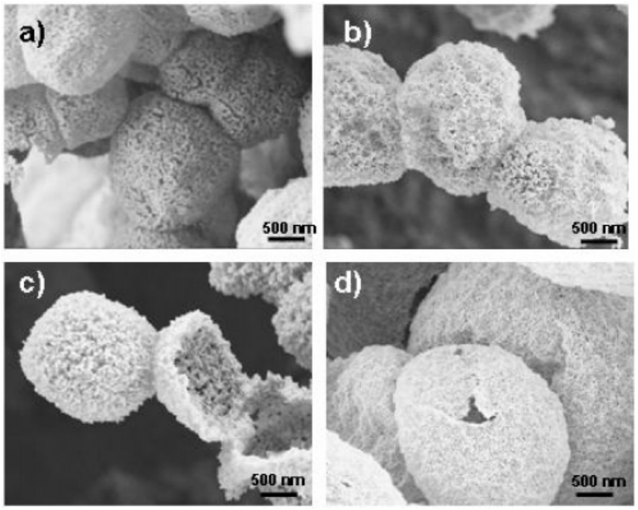


Figure 3. SEM images of (a) NiO, (b) Co_3O_4, (c) CeO_2, and (d) MgO hollow spheres.

the precursor metal salts are water soluble. This was proven for several metal salts, among them iron, nickel, cobalt, cerium, and magnesium salts. In this series, the charge and counteranion of the metal salts seem not to have a crucial influence on the size and morphology of the corresponding metal oxide hollow spheres (Figures 2 and 3).

For the present experimental parameters, the hollow spheres exhibit diameters of around 1 μm. The SEM micrographs (Figure 3) further reveal that the shell is formed out of aggregated metal oxide nanoparticles. It can also be seen that the smooth and spherical morphology of the carbon particles is not entirely transferred to the metal oxide hollow spheres. This can be attributed to structural changes involved in the formation and crystallization of the metal oxide shell during calcination.

The obtained hollow spheres were further investigated by means of TEM. Figure 4 displays the micrographs of samples from different metal oxides and the corresponding electron diffraction pattern after calcination for 4 h at 550 °C. All micrographs show almost spherical hollow structures, even though a closer look reveals some rough edges on the surface. As was seen in the SEM pictures, the shell is composed of aggregated nanoparticles of the metal oxides, yielding an inherent porosity of the shell. The thickness of the metal oxide shell is around 100 nm for a glucose:metal ratio of 5:1.

All electron-diffraction experiments showed high crystallinity of the materials.

The composition of the shells was also followed by XRD measurements. Figure 5 shows the diffraction patterns of the particles after calcination.

The indexing of the peaks reveals that the shells are composed of pure Fe_2O_3, NiO, Co_3O_4, and CeO_2, respectively. No crystalline peaks were observed before calcination, which confirms that after hydrothermal treatment, the metal ions are evenly dissolved in the hydrophilic shell of the carbon particles or dispersed in the shell as amorphous clusters. Note that the formation of iron(III) oxide, cobalt-(II,III) oxide, and cerium(IV) oxide from formerly used metal(II) salts and cerium(III) nitrate, respectively, indicate that these metal ions undergo at least partial oxidation during calcination.

Because the hollow spheres are composed of nanoparticles of the corresponding metal oxides, a high surface area can be expected. This was proven by BET analysis. The surface areas of the different metal oxides at different glucose:metal salt concentrations are given in Table 1.

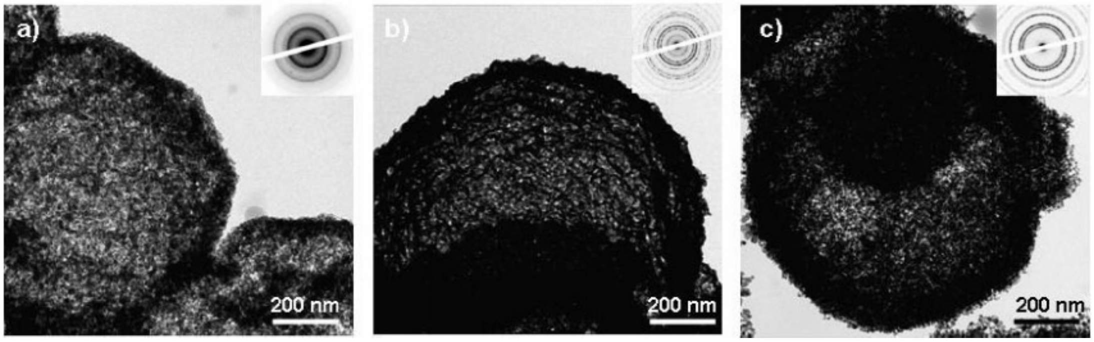


Figure 4. TEM images and selected area electron diffraction of (a) Fe_2O_3, (b) NiO, and (c) Co_3O_4 hollow spheres.

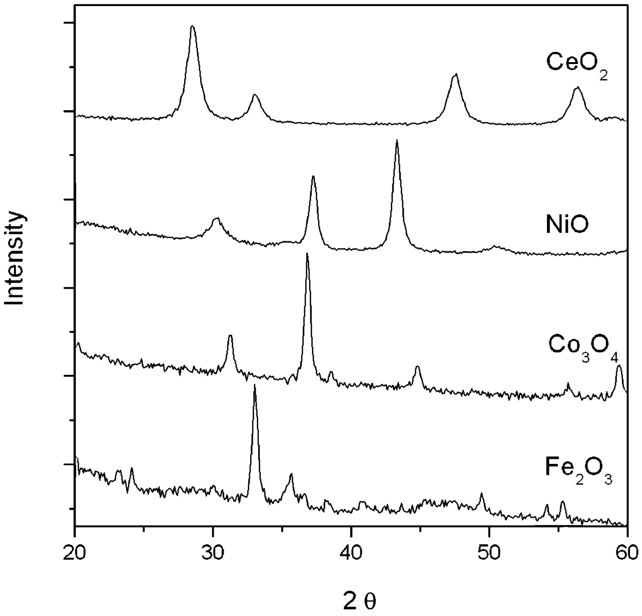


Figure 5. XRD diagrams of hollow spheres calcined for 4 h at 550 °C.

Table 1. BET Surface Areas of Various Metal Oxide Hollow Spheres

material (glucose:metal salt molar ratio)	BET surface area (m^2/g)
Fe$_2$O$_3$ (15:1)	83.5
Fe$_2$O$_3$ (10:1)	38.1
Fe$_2$O$_3$ (5:1)	22.0
Co$_3$O$_4$ (5:1)	26.3
NiO (5:1)	35.6
CeO2 (10:1)	75.2

The BET surface areas of samples made with the comparable glucose:metal salt molar ratios (5:1) show a slight increase in the surface area from iron(III) oxide (22.0 m^2/g) to cobalt(II,III) oxide (26.3 m^2/g) and nickel(II) oxide (35.6 m^2/g). These increases in the surface area do not follow the solid-state densities but are rather to be explained by surface stabilization effects throughout the deposition/carbonization process.

For a particular metal oxide, the surface area of hollow spheres can be controlled by varying the glucose-to-metal ratios, as can be seen for three Fe$_2$O$_3$ samples prepared from different glucose:Fe^{2+} ratios. From molar ratios 5:1 to 15:1, the surface area increases from 22.0 to 83.5 m^2/g. This can be explained with smaller nanoparticle sizes for lower amounts of metal salts with respect to the carbohydrate concentration. A Scherrer analysis of Fe$_2$O$_3$ samples made with different glucose:metal salt ratios revealed nanoparticles sizes from 16 nm for the lowest (5:1) to 22 nm for the highest (15:1) iron salt concentration (as evaluated from the (104) peak and with a correction factor of 1).

Because the size of the carbon spheres does not depend on salt concentration, the relative change in the metal salt concentration not only makes the constituting nanoparticles smaller but should also result in a variation in shell thickness. Figure 6 depicts the iron oxide hollow spheres made from solutions with different glucose:metal molar ratios. Lower metal concentrations lead to a light packing of the iron oxide nanoparticles and a thin shell, whereas an increase in the metal concentration yields a much denser packing and the formation of a robust and thicker shell.

The variety of metal salts that can be used to prepare metal oxide hollow spheres in a one-pot synthesis is defined by the fact that they must be water soluble. It is noteworthy to point out that some variations in the synthesis had to be carried out when metal salts with high oxidation potentials were used. These salts can be reduced by the aldehyde groups of the carbohydrate prior to the dehydration and condensation, which yielded a different carbonization and growth mechanism. This was, for example, shown reasonably for silver salts.[18]

In Figure 7, SEM micrographs and XRD measurements of the products made from glucose/copper salt mixtures before and after calcination are shown. The uncalcined samples show different types of morphologies: aside from the usual carbon spheres, a large number of rods are observed. XRD measurements further reveal the formation of elemental copper in the samples.

The formation of rods indicates a significant change in the colloidal growth mechanisms when additional redox reactions between the metal salts and the carbohydrates take place. We presume that the rods are essentially generated by a synergistic reduction/carbonization process, as elucidated for Ag nanocables.[18] After removal of carbon via oxidative calcinations, we observe hollow oxidic tubes beside the hollow spheres. From the XRD measurements it can be concluded that these hollow morphologies are composed of copper oxide, which is presumably formed from elemental copper nanorods during calcination.

To avoid the complexity of such redox reactions throughout carbonization of the carbohydrate, we can replace glucose with nonreducing sucrose as the precursor. In the absence of metal salts, sucrose forms carbon spheres comparable to many other carbohydrates. No difference is observed in the size or shape compared to carbon spheres obtained from

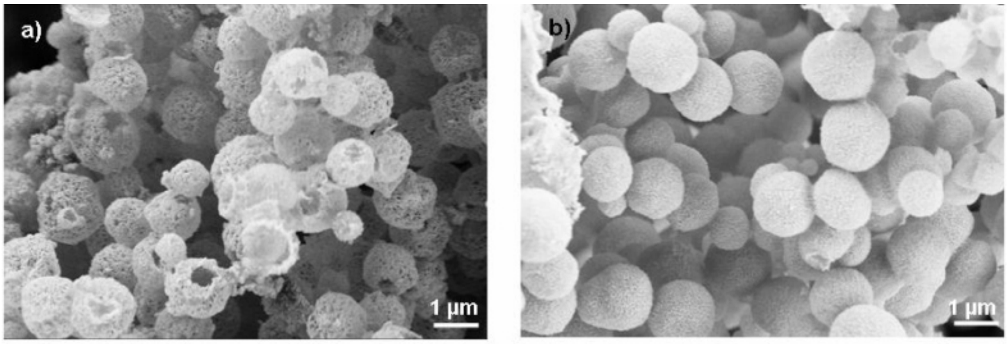


Figure 6. SEM images of Fe$_2$O$_3$ hollow spheres derived from different glucose:Fe^{2+} ratios: (a) 15:1 and (b) 5:1.

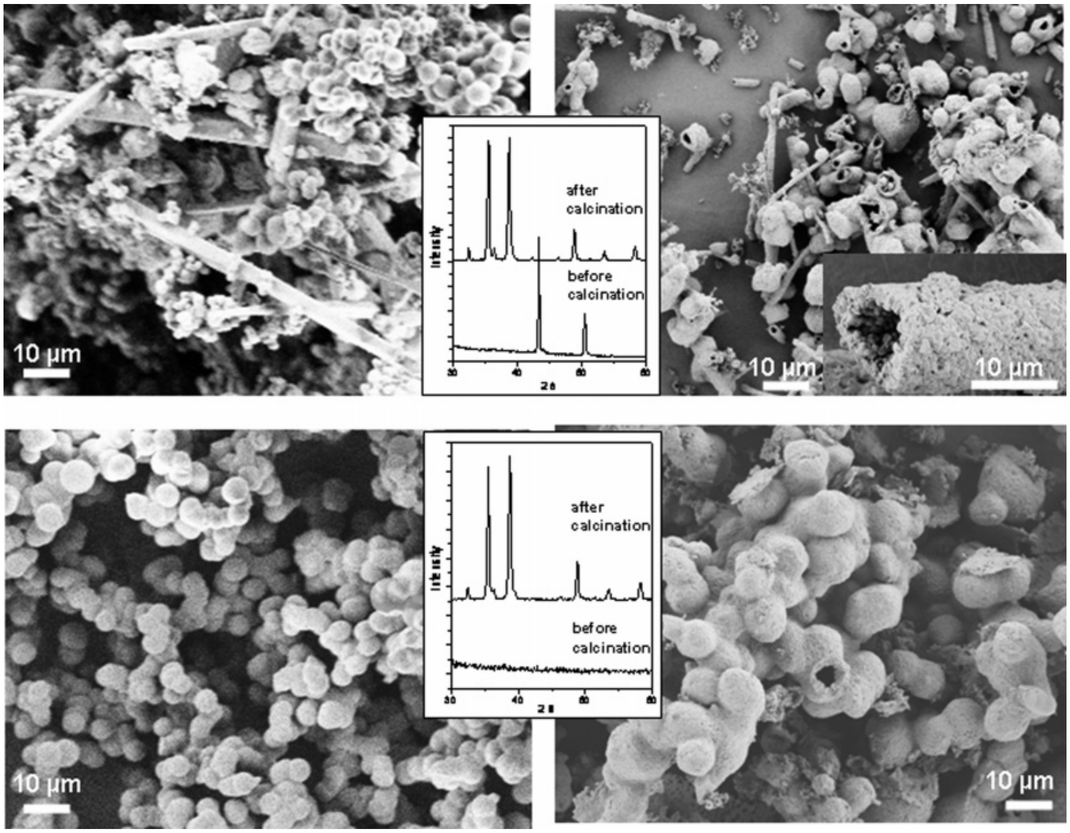


Figure 7. SEM images and XRD diagrams of the products observed before and after calcination from hydrothermally treated glucose/Cu^{2+} mixtures (top row) and sucrose/Cu^{2+} mixtures (lower row).

glucose. XRD measurements of the product with added copper salt indeed show the absence of elemental copper (Figure 7), i.e., the reduction of the copper ions during the reaction can be suppressed. After calcination, hollow spheres of copper oxide are formed, comparable to all other examined systems, as shown by SEM and XRD measurements.

Conclusion

In conclusion, a very simple and scalable pathway towards metal oxide hollow spheres has been explored using hydrothermal synthesis. After the hydrothermal treatment of mixtures of carbohydrates with different metal salts in water in sealed steel autoclaves at 180 °C, carbon spheres with the metal precursors tightly embedded in the microspheres were obtained. The removal of carbon directly results in hollow spheres of the corresponding metal oxide that are composed of nanoparticles with high surface areas. In this report, the synthesis of iron, nickel, cobalt, cerium, magnesium, and copper oxide hollow spheres has been reported. However, we expect that the described synthesis herein can be expanded to further metal oxides because the only prerequisite is that the corresponding metal salts are water soluble, i.e., it represents a generalized synthesis of metal oxide hollow spheres. We therefore believe that this approach is a useful addition to the other current syntheses of hollow spheres by using sol−gel chemistry and coating of spherical objects, especially because most of the metal oxides presented here are not accessible by ordinary sol−gel processes.

Metal oxide hollow spheres have so far found interesting applications, for example, as chemical sensors or in catalysis. We hope that the present observations, including the simplified access and the variation in particle size and surface area, can contribute to further development of the field.

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