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Hierachically porous nanocrystalline cobalt oxide monoliths through nanocasting[†]

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Nanocrystalline cobalt oxide, Co_3O_4, monoliths exhibiting hierarchical bimoidal porosity have been prepared by nanocasting of porous silica monoliths.

Cobalt oxide (Co_3O_4) has found many industrial uses, including anode materials in batteries, as well as catalyst, gas sensor and magnetic materials.[1] In all these applications, a high surface area of the cobalt oxide is needed, which normally is realized through depositing nanoparticles on a porous carrier. A direct synthesis of mesoporous cobalt oxide, and other transition metal oxides for that matter, using surfactants as structure directing agents, is not a straightforward task due to rapid hydrolysis and condensation kinetics and often-encountered changes of the oxidation state of the inorganic precursor. Recently some advances have been made in connection to the surfactant assisted synthesis of ZrO_2 and Al_2O_3 powders exhibiting mesoporosity and macroporosity.[2] However, since the synthesis is under kinetic control, only a portion of the powder shows this feature, which puts a limit on the applicability of this approach. One way to get around the problem of limited overall reproducibility is to use a replication technique, where a porous solid mold is used as a true template. In a series of papers, Ryoo *et al.* described a method to prepare mesoporous carbon by using mesoporous silica with an interconnected pore system, such as SBA-15, as nanocasting molds.[3] The resulting porous carbon obtained after removal of the silica mold by leaching is a negative replica of the host. This type of carbon material can then be used as a mold for further replication to other metal oxides, where the carbon is removed by combustion.[4] Nonetheless, this process is complicated and expensive to scale up. An easier and more economical way to prepare mesoporous metal oxides is a direct replication from silica. A number of different mesoporous oxides have already been prepared in the form of powders.[5] Another related approach utilizing a replication technique is to impregnate the voids between closely packed silica or latex spheres with a metal salt, convert the salt to an oxide and subsequently remove the silica or the latex spheres.[6] In all the above mentioned cases, a mono- or bimodal porosity has been obtained. In some applications, however, and also from a processing point of view, a monolithic structure is preferable. However, until now only a few reports have been available where metal oxide monoliths other than silica have been prepared through direct synthesis *via* an emulsion-based sol–gel route.[7] Very recently, we and others reported on the successful preparation of hierarchically porous, nanocast carbon monoliths.[8] The versatility of the synthesis of silica monoliths exhibiting multimodal, fully interconnected porosity makes these materials highly interesting as molds for other nanocast oxides, since the pore size can be predictively adjusted within a wide range still maintaining a narrow pore size distribution.[9,10]

Here we describe the first successful synthesis of monolithic macro/bimodal mesoporous non-siliceous oxide based on direct nanocasting from silica. Cobalt oxide (Co_3O_4) is used as an example, and the monoliths shown in Fig. 1 were prepared according to Scheme 1. The starting silica monoliths were synthesized according to the procedure described by Nakanishi[10] and exhibited a bimodal interconnected pore structure with macropores with a mean pore diameter of 20 μm and textural mesopores with a mean pore diameter of 15 nm. The poly(ethylene glycol) used in the silica monolith synthesis in order to facilitate spinodal decomposition was removed by exposing the as-synthesized monoliths to treatment with concentrated sulfuric acid, which has been shown to be a straightforward means of retaining the maximum amount of surface silanol groups.[11] A high concentration of surface silanol groups enhances the penetration of the cobalt precursor solution into the mesopores of the silica host. The starting silica monolith[‡] was impregnated with a saturated aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (3.67 g ml^{-1}) by incipient wetness. Cobalt nitrate is a good precursor for cobalt oxide due to its high solubility in water and low decomposition temperature (74 °C). The water is evaporated and at the same time the salt is decomposed to Co_3O_4 by exposing the impregnated monoliths to thermal treatment at 220 °C for 10 h without heating ramp. This procedure led to a 60–70% reduction in the mesopore volume after normalization for differences in mass, indicating a preferential filling of the mesopores of the silica monolith. A rapid drying of the impregnated monoliths is essential for ensuring a homogeneous incorporation of cobalt oxide into the pores of the silica mold, since otherwise the cobalt precursor is transported with the liquid to the external surface of the silica mold due to capillary forces. The impregnation and the heat treatment steps were repeated twice. The composite was subsequently calcined at 550 °C (heating ramp 1 °C min^{-1}) for 6 h (optional).

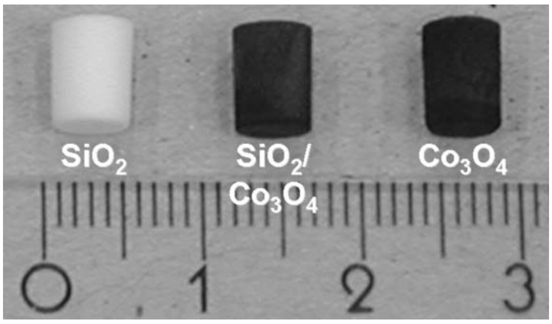
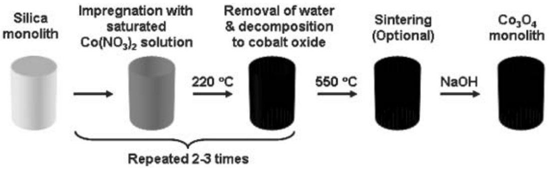


Fig. 1 Silica, composite and cobalt oxide monoliths (scale bar in cm).



Scheme 1 Synthesis procedure for preparation of Co_3O_4 monoliths.

[†] Electronic supplementary information (ESI) available: nitrogen sorption isotherm measured for the Co_3O_4 monolith and the corresponding BJH pore size distribution plot. SEM image of a Co_3O_4/SiO_2 composite. See http://www.rsc.org/suppdata/cc/b4/b405208k/

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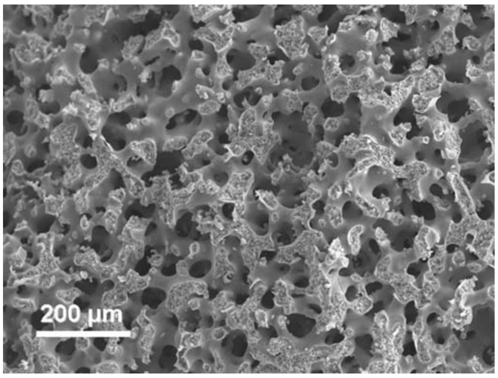

Fig. 2 A representative SEM image of the macroporous Co_3O_4 replica.

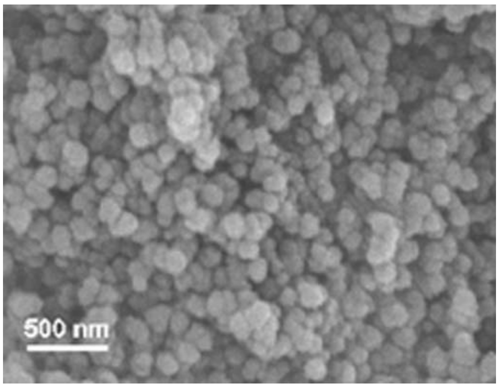

Fig. 3 SEM image of the Co_3O_4 replica wall structure.

The silica portion was subsequently leached out in a 1 M NaOH solution.

Less than 1 wt% silica could be detected in the final cobalt oxide monoliths by EDX analysis, suggesting a virtually complete removal of the silica. A representative scanning electron microscopy, SEM, image (Hitachi S-3500N) of the macropore structure of the cobalt oxide monolith is shown in Fig. 2. The appearance is a direct positive replica of the pore structure of the starting silica monolith, suggesting that the porous walls of the silica monoliths have been evenly impregnated by the cobalt precursor. However, some cobalt oxide particles have formed in the macropores of the starting silica monolith, (see ESI†) although mercury porosimetry measurements indicated no shift of the macropore size ($\sim$20 µm) (results not shown). At higher magnification, Fig. 3, it is clear that the walls are built up from a loose packing of near spherical aggregates with a diameter of about 150 nm. Such aggregates can also be observed in the walls of the host silica monlith[9] and are thus a result of positive replication. Voids between these aggregates give rise to interaggregate pores in the cobalt oxide monolith with a mean pore size of 100 nm as determined by mercury porosimetry. Moreover, the aggregates are built up of fully crystalline Co_3O_4 nanoparticles, about 20 nm in diameter, as can be seen in the transmission electron microscopy, TEM, (Hitachi HF 2000) image shown in Fig. 4.

The crystal structure was also confirmed by X-ray diffraction. The crystallite size as determined by the Debye–Scherer method was 20–40 nm, in good agreement with the TEM results. The loose packing of these particles gives rise to yet another pore size region of about 10 nm, as determined by nitrogen porosimetry according to the $BJH_{desorption}$ algorithm (see ESI†). These particles represent a negative replication of the original silica monolith and have formed in the void space between silica particles, being the primary building blocks of the porous silica monolith. Depending on the calcination temperature, the Co_3O_4 monoliths exhibit a high specific surface area (BET) of 30–70 $m^2 g^{-1}$.

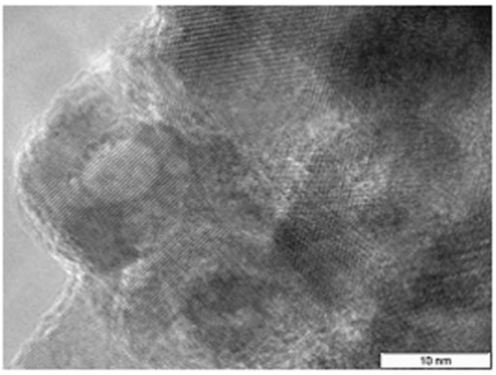

Fig. 4 TEM image of the crystalline primary Co_3O_4 particles.

In summary, we have described a versatile, fully reproducible, means for the preparation of nanocrystalline transition cobalt oxide monoliths exhibiting a multimodal, fully interconnected, hierarchical pore structure. Such materials can be of great interest in a wide variety of applications, including catalysis and sensor applications. The method can also be extended to the preparation of porous monoliths of other transition metal oxides, and these results will be reported shortly elsewhere.

Notes and references

‡ The silica monoliths were prepared by dissolving poly(ethylene glycol) (PEG, M_w = 35 000 g mol^{-1}) in H_2O and HNO_3 (30%). Tetraethyl orthosilicate (TEOS) was then added and the solution was stirred until a clear and homogeneous solution was obtained. The H_2O : HNO_3 : TEOS : PEG(35 000) molar ratio in the final sol was 14.7 : 0.25 : 1: 6.9×10^{-4}. The solution was portioned into cell growth blocks and was allowed to gel and age for 72 h at 40 °C. Solvent exchange in a 1 M NH_4OH solution for 8 h at 90 °C was performed to increase the stability of the monoliths and PEG was removed with treatment in 60% H_2SO_4 together with H_2O_2 for 24 h.[11] Afterwards, the monoliths were neutralized with 0.1 M NH_4OH and water, washed with acetone, and subsequently dried for 24 h at 80 °C.

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