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ORIGINAL PAPER

The "benzyl alcohol route": An elegant approach towards doped and multimetal oxide nanocrystals

Short review and $ZnAl_2O_4$ nanostructures by oriented attachment

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Abstract In this article, the versatility and the potential of the "benzyl alcohol route" for the synthesis of multimetal and doped metal oxides are highlighted in the first part of the manuscript. Among the presented examples, some materials have not been accessible by other solution syntheses and could so far only be obtained through solid state reactions. The second part describes the synthesis and characterization of 5–6 nm $ZnAl_2O_4$ nanoparticles which form flower-like aggregates through the oriented attachment crystallization mechanism.

Keywords Nanocrystals · Metal oxides · Nonaqueous synthesis

1 Introduction

Various liquid phase chemical approaches have been introduced in the past decades for the synthesis of metal oxide nanoparticles [9, 15, 21, 32, 43]. They were reported extremely successful for the production of simple oxides (e.g. binary). Indeed, dozens of routes for the production of titanium and zinc oxide nanoparticles can be found in the recent literature. In contrast, approaches leading to the formation of multimetal and doped metal oxides by soft chemistry approaches are rarely reported and many oxides can still only be obtained through solid state reactions. The main reason resides in the difficulty to match the reactivity of the different metal precursors in solution, which prevents the formation of multimetal phases or the homogeneous doping of simple oxides [43]. This is especially true for aqueous routes (e.g. sol–gel) since the hydrolysis rates are generally fast and strongly depend on the metal center [18]. To circumvent this problem, numerous studies were conducted in the aim of modifying the metal complexes, such as metal alkoxides, in order to control and to decrease their reactivity [48]. Nonaqueous sol–gel routes were introduced for the same purpose. In fact, the reactivity of the metal oxide precursors is greatly decreased under water exclusion, thus making it easier to control the metal oxide formation [25, 51]. Nonaqueous routes were successfully applied for the synthesis of various metal oxide nanoparticles [19, 43], hybrid materials [36] and also for the growth of metal oxide thin films by atomic layer deposition [5]. Moreover, they gave access to various multimetal and doped oxides.

In spite of the recent progress in nanoparticle research, it is not yet possible to prepare a certain compound on the nanoscale with a desired composition, structure, size and shape, intentionally and in a predicted way. One of the reasons is the fact that it is not yet possible to predict the reactivity of metal complexes in a particular solvent. Moreover, the metal oxide formation is influenced by various additional effects such as intermediate products formed during the reaction, side reactions and catalytic effects of the metal centers, the metal oxide seeds and early formed nanoparticles. Therefore, the synthesis of new materials by nonaqueous sol–gel routes, and other liquid phase approaches, are still based on simple trial-and-error

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experiments. To go beyond such an approach, a detailed knowledge on the different effects influencing the metal oxide formation must be acquired. One of the ways to progress in this direction is through the generalization of synthesis approaches and by studying the chemical mechanisms taking place during metal oxide formation. Since the most general and versatile approach to metal oxide synthesis is probably the reaction of metal complexes in benzyl alcohol [21, 29, 36, 43] a detailed study of this reaction approach might solve many of the questions enumerated above and perhaps lead to the synthesis of new materials in a more predictable way.

In this articles we are going to shortly introduce the "benzyl alcohol route" and its use for the production of multimetal and doped metal oxide nanostructures. In the second part of the manuscript the synthesis and characterization of $ZnAl_2O_4$ complex nanostructures following this method are going to be described.

2 The "benzyl alcohol route"

A particularly attractive reaction approach for the synthesis of crystalline metal oxide nanoparticles is the "benzyl alcohol route". It is a one pot reaction that, based on the reaction of various metal complexes (e.g. chlorides, alkoxides, acetates, acetylacetonates) in benzyl alcohol leads to metal oxide formation in a controlled way. Hereby the latter is acting as solvent, ligand and reactant. The syntheses of titanium, tungsten and vanadium oxides were first reported by Niederberger et al. in 2002 by reacting metal chlorides (i.e. titanium, tungsten and vanadium) with benzyl alcohol between 40 and 120 °C, i.e. well below the boiling point of benzyl alcohol (~ 205 °C) [22, 23]. Just two years later it was reported that the reaction of various metal alkoxides in benzyl alcohol permitted to synthesize various binary and ternary metal oxide nanoparticles [28, 30, 37–39, 41]. In 2009 the number of metal oxides synthesized following this methodology is larger than 50, pointing out the versatility of the approach. The main chemical reactions involved in the metal oxide formation, from the reaction of metal complexes in benzyl alcohol, are the alkylhalide elimination, ester elimination, ether elimination, and the C–C bond formation between benzylic alcohols and alkoxides [19, 25, 29, 43]. It is evident that the ligand plays the most important role in determining the reaction pathway, nevertheless the nature of the metal center can also dramatically influence the chemistry and the characteristics of the final material. The most significant example involves the reaction of metal alkoxides in benzyl alcohol. As a matter of fact, it was demonstrated that the reaction of various metal alkoxides such as $Ti(OiPr)_4$, $Zr(OiPr)_4{\cdot}HOiPr$, $Hf(OEt)_4$, $Nb(OEt)_5$ and $Sn(OtBu)_4$ lead to the elimination of an ether together with the metal oxide formation. However, in the case of $BaTiO_3$ and $NaNbO_3$ the presence of a basic species (Ba and Na alkoxides) was the prerequisite for another mechanism involving a C–C bond formation between alkoxy ligands and benzyl alcohol [13, 25]. Such a mechanism was also demonstrated for metals with high Lewis acidity, such as many rare earth elements (Y, Ce, Gd, Nd, Sm), which can directly catalyze this Guerbet-like reaction [16, 25, 26, 40]. Moreover, the yttrium and some lanthanides (Gd, Nd, Sm) isopropoxides were able to catalyze, in addition to the C–C bond formation between isopropoxy ligands and benzyl alcohol, two additional reactions leading to oxidation of benzyl alcohol to benzoic acid and finally to the formation of oxide-benzoate hybrid nanostructures instead of pure inorganic nanoparticles. The morphological and structural differences between TiO_2, $BaTiO_3$, $NaNbO_3$ and CeO_2 on one, and the rare earth lamellar organic–inorganic hybrid nanostructures on the other side are also reflected in small, but crucial variations in the organic reaction pathways, pointing out the importance of mechanistic studies in nanomaterial synthesis.

The versatility of nonaqueous routes to oxide nanoparticles was already highlighted in various reviews and will not be further discussed here [21, 26, 27, 29, 43]. In this work we will focus on the peculiar features of the "benzyl alcohol route" that make it possible to synthesize homogeneous ternary, multi-metal and doped oxide nanoparticles.

The different reactivity of metal complexes towards a specific solvent complicates the synthesis of oxides containing two or more metals. In organic solvents (and especially in benzyl alcohol) it is easier to match the reactivity of the metal complexes and of the dopants in comparison to aqueous systems. This is a prerequisite for obtaining single-phase products. Table 1 enumerates the different multimetal oxide nanostructures that have been synthesized in benzyl alcohol. Crystalline titanate, niobate, aluminate nanostructures and other important multimetal oxides are readily obtained at temperatures varying from 180 to 275 °C. From Table 1 it appears evident that various metal complexes can be employed ranging from simple inorganic (e.g. chlorides and nitrates) to metal organic (e.g. acetates, acetylacetonates and alkoxydes) complexes. For example, Xiao et al. [54] showed that the reaction of $Zn(NO_3)_2{\cdot}H_2O$ and NH_4VO_3 in benzyl alcohol leads to ZnV_2O_4 hollow spheres having a complex nanostructure, highlighting that simple and inexpensive precursors can also be used (Fig. 1 a, b). The reaction of calcium methoxide and aluminum isopropoxide in benzyl alcohol lead to flower like complex nanostructures of $CaAl_4O_7$ consisting of thin platelets or needles as shown in Fig. 1c [17]. About 5–10 nm $YNbO_4$ nanoparticles (Fig. 1d) can be synthesized from $Y(acac)_3{\cdot}xH_2O$ and $NbCl_5$ [56]. Five nanometers

Table 1 Ternary and multi metal oxide nanoparticles synthesized in benzyl alcohol

Metal oxide	Precursors	Shape	Ref.
Antimony tin oxide	$SnCl_4$ + $SbCl_3$	Spherical	[49]
$BaAl_2O_4$	Ba + Al(O*i*Pr)$_3$	Flower like	[17]
$BaTiO_3$	Ba + Ti(O*i*Pr)$_4$	Spherical	[3, 28, 30]
$BaZrO_3$	Ba + Zr(O*i*Pr)$_4$·HO*i*Pr	Slightly elongated	[30]
(Ba,Sr)TiO_3	Ba + Sr + Ti(O*i*Pr)$_4$	Spherical	[28]
$CaAl_4O_7$	Ca(OMe)$_2$ + Al(O*i*Pr)$_3$	Flower like	[17]
$CdIn_2O_4$	Cd(ac)$_2$ + In(O*i*Pr)$_3$	Spherical	[4, 52]
$InNbO_4$	In(acac)$_3$ + $NbCl_5$	Spherical	[55, 56]
Indium tin oxide	In(acac)$_3$ + Sn(O*t*Bu)$_4$	Spherical	[1, 2]
$La_{1-x}A_xMnO_3$ (A = Ca, Sr, Ba)	Various	–	[50]
$LiNbO_3$	Li + Nb(OEt)$_5$	–	[30]
$MnNb_2O_6$	Mn(acac)$_3$ + $NbCl_5$	–	[56]
$NaNbO_3$	Na + Nb(OEt)$_5$	Spherical	[14]
$NaTaO_3$	Na + Ta(OEt)$_5$	–	[14]
$SrAl_4O_7$	Sr + Al(O*i*Pr)$_3$	Flower like	[17]
$SrTiO_3$	Sr + Ti(O*i*Pr)$_4$	Spherical	[28]
$YNbO_4$	Y(acac)$_3$·xH$_2$O + $NbCl_5$	Spherical	[56]
$ZnAl_2O_4$	Zn(ac)$_2$ + Al(O*i*Pr)$_3$	Spherical	This work
ZnV_2O_4	Zn(NO$_3$)$_2$·H$_2$O + NH_4VO_3	Hollow spheres	[54]

ac = acetate, acac = acetylacetonate

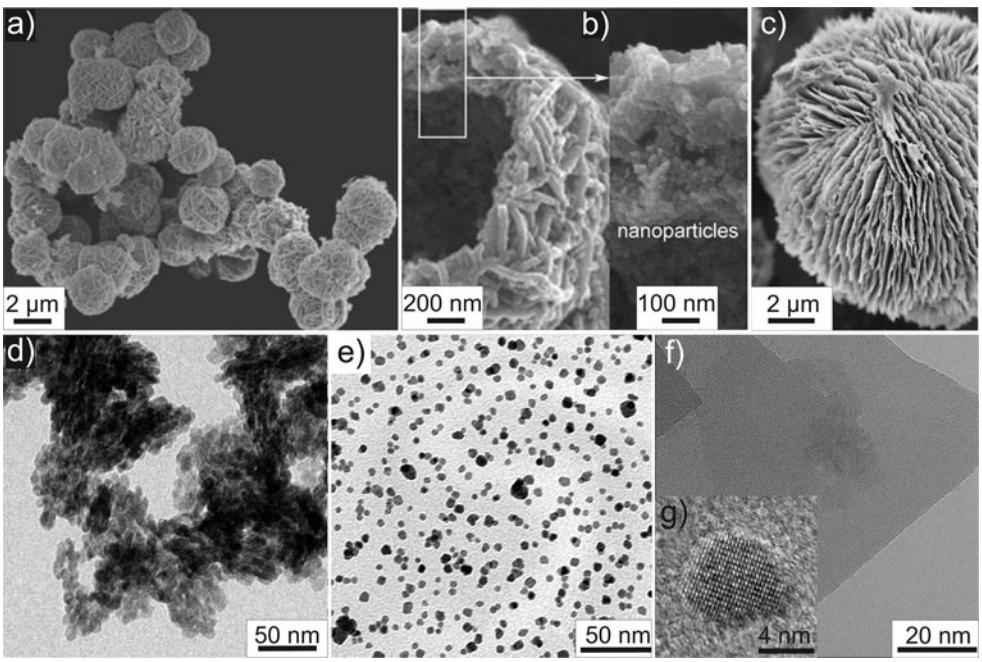

Fig. 1 **a**, **b** SEM images of ZnV_2O_4 hollow spheres reproduced with permission from reference [54]. **c** SEM of $CaAl_4O_7$ nanostructures [17]. **d** TEM of $YNbO_4$ nanoparticles reproduced with permission from reference [56]. **e** TEM of indium tim oxide nanoparticles reproduced with permission from reference [2]. **f** HRTEM of the ending of a $CaAl_4O_7$ nanostructure shown in c) [17]. **g** HRTEM of a (Ba,Sr)TiO_3 nanoparticle [28]

Indium tin oxide nanoparticles (Fig. 1e) are obtained from In(acac)$_3$ and Sn(O*t*Bu)$_4$. These last examples highlight the fact that in order to match the reactivity of the metal complexes in benzyl alcohol it is often necessary to employ different ligands for each metal center. As a typical example, solid solution of indium tin oxide nanoparticles could

Table 2 Doped metal oxide nanoparticles synthesized in benzyl alcohol

Metal oxide	Precursors	Shape	Ref.
Mn-/Cr-doped HfO_2	$Hf(OtBu)_4$ + $Mn(acac)_3$, $Mn(acac)_2$, $Mn(ac)_2$ or $Cr(acac)_3$	Spherical	[47]
Co-/Fe-doped TiO_2	$Co(acac)_2$, $Fe(acac)_3$, $Ti(OiPr)_4$, $TiCl_4$	Spherical or well-faceted	[10]
Mn-/Co-doped ZnO	$Zn(ac)_2$ + $Mn(oleate)_2$ or $Co(ac)_2$	Nanorods and Nanowires	[6]
Mn-/Co-doped ZnO	$Zn(acac)_2{\cdot}xH_2O$ + $Mn(acac)_2$ or $Co(acac)_2$	Nanorods	[11]
Eu-doped ZrO_2	$Zr(OiPr)_4{\cdot}HOiPr$ + $Eu(acac)_3{\cdot}xH_2O$	Spherical	[31]
Mn-/Cr-doped ZrO_2	$Zr(OiPr)_4{\cdot}HOiPr$ + $Mn(acac)_3$, $Mn(ac)_2$ or $Cr(acac)_3$	Spherical	[7, 47]

ac = acetate, acac = acetylacetonate

not be obtained using In(III) alkoxide instead of $In(acac)_3$ because in this case, the different reactivity of the two metal complexes does not permit the formation of a solid solution [20, 42]. The particles size and shape greatly differ from one system to another, but within a particular system the materials are rather monodisperse.

Finally, the high crystallinity of the as synthesized multimetal oxide nanostructures is demonstrated by the Fig. 1f, g. They show, respectively, HRTEM images of $CaAl_4O_7$ platelets that build up the flower like structures shown in Fig. 1c and a 6 nm sized $(Ba,Sr)TiO_3$ nanoparticle.

Nonaqueous reaction conditions seem to be particularly suitable for doping of binary metal oxide nanoparticles as well (Table 2). The most studied systems are the non-magnetic binary oxides (e.g. ZnO, ZrO_2, HfO_2) doped with magnetic impurities (e.g. Co, Mn) for application in e.g. spintronic. The synthesis approach proved to be rather robust also in this case and led to the homogeneous doping of various binary oxides with magnetic ions even at relatively high dopant concentration. The largest effective doping concentration (17%) was obtained for HfO_2 doped with Mn from $Mn(acac)_3$. In almost all these cases a detailed characterization of the doping homogeneity and behavior was performed in order to correlate the structural, doping and magnetic properties [6, 47].

3 $ZnAl_2O_4$ nanostructures by oriented attachment

Zinc aluminate, a catalyst and catalyst support, can be obtained at the nanoscale by soft chemistry routes and by making use of the Kirkendall effect, allowing the formation of well defined nanotubes starting from an anodized aluminum oxide template impregnated with zinc oxide, or from zinc oxide nanowires coated with alumina [12, 53]. The solvothermal reaction (T = 250 °C) of $Zn(ac)_2$ and $Al(OiPr)_3$ in benzyl alcohol for two days leads to the formation of $ZnAl_2O_4$ nanostructures. The X-ray diffraction pattern (XRD) is typical for the spinel $ZnAl_2O_4$ structure (Fig. 2). The width of the reflections speak for a nanostructured material with an average crystallite size of 10 nm as estimated using the Scherrer equation. The TEM

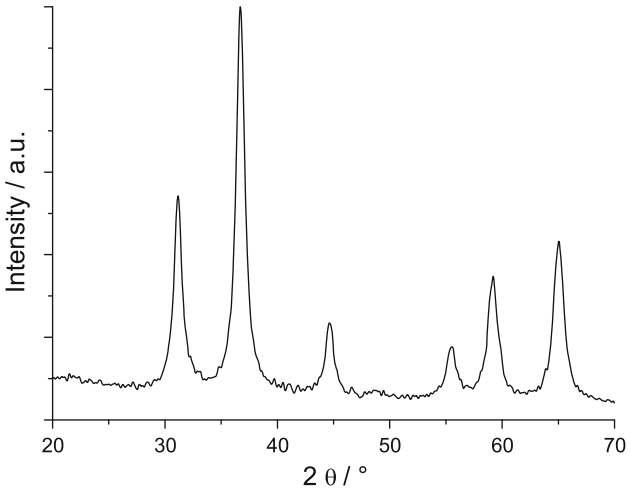

Fig. 2 XRD pattern of $ZnAl_2O_4$ nanocrystals

observation reveals that the as synthesizes $ZnAl_2O_4$ forms flower-like nanostructures of around 30 nm in size (Fig. 3a). High resolution images recorded from these nanostructures reveal that they are constituted of well defined 5–6 nm primary particles (Fig. 3b). The size of these primary particles is therefore slightly smaller than the crystalline size extracted from XRD measurements. Analysis of the lattice fringes reveals that the planes of neighboring nanoparticles coincide. Furthermore, the power spectrum of the whole image resembles that of a single crystal (inset of Fig. 3b; the zone axis is [111]). This observation indicates that the flower-like aggregates are formed by an oriented attachment crystallization mechanism. Oriented attachment involves the interaction of adjacent particles and their fusion, leading to nanostructured aggregates that appear as single crystals which often contain defects at the interface where the primary particles fuse. This mechanism was firstly reported by Penn and Banfield on the study of aggregation of anatase nanoparticles under hydrothermal conditions [33–35]. After these first reports many other have followed for many other systems, mostly for metal oxide nanoparticles (cf. e.g. [44–46, 57]). Such a non-classical crystallization mechanism was recently reviewed by Coelfen et al. [8, 24].

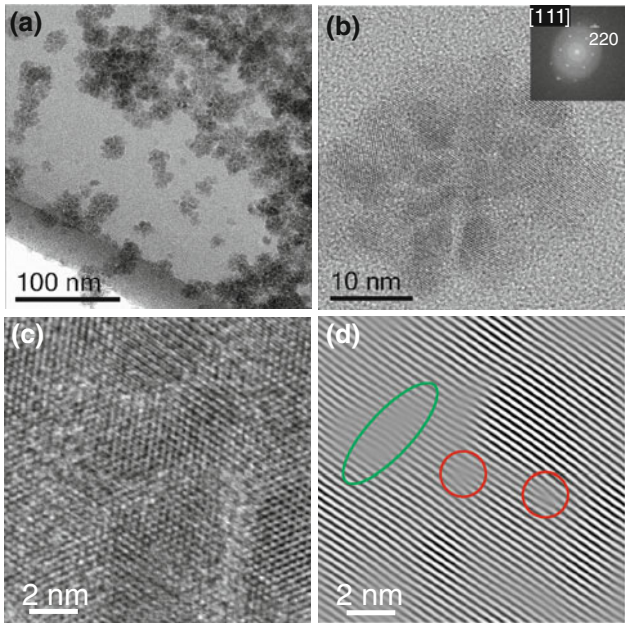

Fig. 3 TEM images of the $ZnAl_2O_4$ nanostructures. **a** Overview, **b** high resolution images. *Inset* power spectrum of **b** the zone axis is the [111]. **c** detail of the HRTEM image in **b** used for the Fourier analysis **d** using the $\bar{2}20$ reflection. *Red circles* show dislocations and the *green circle*- a zone of non perfect orientational matching between planes of two attached nanoparticles. (Color figure online)

In order to verify this hypothesis, Fourier filtered images using the $\bar{2}20$ reflection of the power spectrum shown in the inset of Fig. 3b were calculated. For better clarity only a portion of the image is shown. Figure 3c and d present a detail of the HRTEM image in b and the corresponding filtered image using the $\bar{2}20$ reflection. In the FFT filtered image, dislocations (red circles) and zones where particles are not perfectly attached (e.g. green ellipsoid) are easier to see. These defects are typical for the oriented attachment crystallization mechanism similarly to the case of tungstite nanoplatelets [46].

4 Conclusions

In this article the versatility and the potential of the "benzyl alcohol route" for the synthesis of multimetal and doped metal oxides were highlighted. Among the examples cited some of the materials are not accessible by other solution synthesis but only by solid state reactions. The second part of the manuscript described the synthesis and characterization of 5–6 nm $ZnAl_2O_4$ nanoparticles, which form flower-like aggregates by the oriented attachment crystallization mechanism.

This article brings further confirmation on the fact that the "benzyl alcohol route" is the most general, versatile and widely applicable approach for the synthesis of crystalline multimetal and doped metal oxide nanostructures in solution and this at relatively low temperature. Finally, additional studies are still needed on the further generalization of the "benzyl alcohol route" and on the growth mechanisms. Indeed, they might permit to go beyond the trial-and-error approach for the synthesis of new materials.

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