Journal of Solid State Chemistry 181 (2008) 1571–1581

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Nonaqueous synthesis of metal oxide nanoparticles: Short review and doped titanium dioxide as case study for the preparation of transition metal-doped oxide nanoparticles

Igor Djerdj [a,*], Denis Arčon [b,c], Zvonko Jagličić [d,e], Markus Niederberger [a,*]

[a] ETH Zürich, Department of Materials, Wolfgang-Pauli-Strasse 10, 8093 Zürich, Switzerland
[b] Institute Jožef Stefan, Jamova 39, 1000 Ljubljana, Slovenia
[c] Faculty of Mathematics and Physics, University of Ljubljana, Jadranska 19, 1000 Ljubljana, Slovenia
[d] Institute of Mathematics, Physics and Mechanics, Jadranska 19, 1000 Ljubljana, Slovenia
[e] Faculty of Civil and Geodetic Engineering, University of Ljubljana, Jamova 2, 1000 Ljubljana, Slovenia

ARTICLE INFO

Article history:
Received 8 February 2008
Received in revised form
31 March 2008
Accepted 11 April 2008
Available online 30 April 2008

Keywords:
Nonaqueous synthesis
Metal oxides
Nanoparticles
Doped titania

ABSTRACT

The liquid-phase synthesis of metal oxide nanoparticles in organic solvents under exclusion of water is nowadays a well-established alternative to aqueous sol–gel chemistry. In this article, we highlight some of the advantages of these routes based on selected examples. The first part reviews some recent developments in the synthesis of ternary metal oxide nanoparticles by surfactant-free nonaqueous sol–gel routes, followed by the discussion of the morphology-controlled synthesis of lanthanum hydroxide nanoparticles, and the presentation of structural peculiarities of manganese oxide nanoparticles with an ordered Mn vacancy superstructure. These examples show that nonaqueous systems, on the one hand, allow the preparation of compositionally complex oxides, and, on the other hand, make use of the organic components (initially present or formed *in situ*) in the reaction mixture to tailor the morphology. Furthermore, obviously even the crystal structure can differ from the corresponding bulk material like in the case of MnO nanoparticles. In the second part of the paper we present original results regarding the synthesis of dilute magnetic semiconductor TiO_2 nanoparticles doped with cobalt and iron. The structural characterization as well as the magnetic properties with special attention to the doping efficiency is discussed.

1. Introduction

Most of the research in the broad field of *Nanoscience* is dedicated to the development of synthesis routes to nanoparticles and nanostructures. These efforts gave access to nanomaterials with a wide range of compositions, monodisperse crystallite sizes, unprecedented crystallite shapes, and with complex assembly properties. But in spite of all the progress, the most synthesis methodologies were found on an empirical basis, i.e., by trial-and-error experiments, representing isolated efforts without any generally valid basic concepts or mechanistic principles that would allow a rational synthesis strategy. The synthetic chemist is still far away from preparing a certain compound on the nanoscale with a desired composition, structure, size and shape, or even properties, intentionally and in a predicted way. The reasons for this major limitation are manifold and in here we will discuss some of these issues in the context of liquid-phase routes to metal oxide nanoparticles, because their synthesis and application is of particular scientific and technological interest.

In contrast to the traditional high temperature preparation of bulk metal oxides, involving the reaction of a mixture of powders, the use of liquid-phase routes bears the advantage that it is possible to obtain metastable materials, to achieve superior compositional homogeneity, and to influence the particle morphology during the chemical transformation of the molecular precursor to the final oxidic network [1]. Especially aqueous sol–gel chemistry was highly successful in the synthesis of bulk metal oxides [2]. However, it turned out that a specific synthesis route, which worked well for the bulk oxide, cannot directly be adapted to its corresponding counterpart on the nanoscale. The reason lies in the fact that aqueous sol–gel chemistry typically leads to amorphous precipitates that are transformed into the desired crystalline material by applying a calcination step. Due to uncontrolled crystal growth, this temperature treatment to induce crystallization is not a viable option for size- and shape-controlled nanoparticle synthesis. Furthermore, aqueous sol–gel chemistry is rather complex, mainly due to the high reactivity of the metal

---

[*] Corresponding authors. Fax: +41 44 632 11 01.
E-mail addresses: igor.djerdj@mat.ethz.ch (I. Djerdj), markus.niederberger@mat.ethz.ch (M. Niederberger).

0022-4596/$ - see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jssc.2008.04.016

oxide precursors and the double role of water as ligand and solvent, complicating the synthesis of small structures. Nevertheless, several recent examples reported in the literature indicate that it is in general possible to prepare metal oxide nanoparticles in aqueous medium in a controlled way given that the experimental conditions are strictly kept [3–6].

A simple way to circumvent many problems of aqueous chemistry is to perform the synthesis procedure in organic solvents under exclusion of water. The rapidly growing number of publications in this field suggests that these so-called nonaqueous (or nonhydrolytic) processes are particularly successful for the size- and shape-controlled preparation of colloidal inorganic nanoparticles [7–9]. In surfactant-controlled approaches the precursor molecules are transformed into the nanocrystallites in the presence of stabilizing surfactants in a typical temperature range of 250–350 °C [7,8,10], whereas solvent-directed processes just involve the reaction of metal oxide precursor(s) with a common organic solvent and usually take place at lower temperature (50–250 °C) [11–13]. The small number of reactants (precursor and solvent) makes it possible to study the chemical mechanisms involved in metal oxide formation through the characterization of the organic by-products [11]. Parallel to the formation of the inorganic nanoparticles, also the initial organic species (i.e., solvent and/or the organic part of the precursor) undergo transformation reactions. In many cases, the formation of the organic compounds can easily be correlated to the growth of the inorganic nanoparticles, which means that chemical reaction pathways for inorganic nanoparticles can be elaborated based on the organic side reactions [11,14]. The main function of the organic species is to act as oxygen source for the oxide formation, however they are actively involved during all stages of particle growth and crystallization, strongly influencing the composition, size, shape, and surface properties of the nanocrystals [14].

Another important advantage of nonaqueous sol–gel processes in comparison to aqueous systems is the accessibility of ternary, multi, and doped metal oxide nanoparticles [13]. The different reactivity of metal oxide precursors towards a specific solvent complicates the synthesis of oxides containing two or more metals. In organic solvents it is easier to match the reactivity of the metal oxide precursors and of the dopants in comparison to aqueous systems, which is crucial for obtaining phase pure products.

This article is divided into several sections. In the first part we give a short overview of nonaqueous surfactant-free sol–gel routes, including a presentation of ternary metal oxide nanoparticles synthesized by these methodologies and some general mechanistic principles regarding the chemical pathways leading to oxidic nanoparticles, followed by the morphology-controlled preparation of lanthanum hydroxide nanoparticles as an example that shows that also organic species formed *in situ* during the reaction course may play a crucial role in determining the crystal shape. Anisotropic crystallite growth can be induced by organic species that are not initially present in the reaction mixture, but formed *in situ*, and therefore the study of all the organics in nonaqueous reaction systems is a prerequisite on the way to completely understand the formation of nanoparticles on a molecular level. The third section reports on manganese oxide nanoparticles with an unusual superstructure exhibiting superparamagnetism. This example nicely illustrates how the structural and physical properties of nanoparticles can differ from the corresponding bulk material. Finally, doping of titania nanoparticles with transition metal ions and their magnetic properties is described.

2. Experimental details

2.1. Materials

Titanium tetrachloride (99.995+ %), titanium tetraisopropoxide (99.999%), iron(III) acetylacetonate (99.9+ %), cobalt(II) acetylacetonate (97%), anhydrous benzyl alcohol (99.8%), and 2-butanone (99+ % spectrophotometric grade) were obtained from Aldrich and used without further purification. The solvothermal treatment was performed in Parr acid digestion bombs with 45 ml Teflon cups.

2.2. Synthesis

All synthesis procedures were started under argon atmosphere in a glovebox. The experimental details for obtaining manganese oxide and lanthanum hydroxide nanoparticles are described in Refs. [15,16], respectively. 3 mol% Co/Fe-doped titania samples were prepared by mixing the corresponding Co/Fe precursor [$Co(acac)_2$/$Fe(acac)_3$] with either 0.5 ml of $Ti(OiPr)_4$ or 0.5 ml of $TiCl_4$. This mixture was then dissolved in 20 ml of the organic solvents: benzyl alcohol, 2-butanone, or a 1:1 vol. mixture thereof (10 ml benzyl alcohol and 10 ml 2-butanone). The mixing of the precursors with the solvent was directly performed in the 45 ml Teflon cups of the acid digestion bombs. The autoclave was taken out of the glovebox and heated in a furnace at 200 °C for 3 days. The resulting suspensions were centrifuged to separate the precipitate from the mother liquid. Excess organic impurities were removed by repeated washing steps in 10 ml of high-grade purity ethanol and subsequently dried in air at 60 °C.

2.3. Characterization

X-ray powder diffraction (XRD) patterns were measured in reflection mode with Cu$K\alpha$ radiation on a X'Pert PRO diffractometer (PANalytical manufacturer) equipped with a X'Celerator detector. The instrumental contribution to the peak broadening caused by instrumental aberrations was removed by the deconvolution method with highly crystalline NIST SRM 660a LaB_6 powdered sample as a standard. The analysis of the XRD patterns was done following a well-established Rietveld procedure using the program FULLPROF [17]. Transmission electron microscopy (TEM) measurements were performed on a Zeiss EM 912Ω instrument at an acceleration voltage of 120 kV, while high-resolution transmission electron microscopy (HRTEM) characterization together with energy-dispersive X-ray spectroscopy (EDX) was done using a Philips CM200-FEG microscope (200 kV, $Cs = 1.35$ mm). For TEM characterization, one drop of the dispersion in ethanol from the last washing step was released onto a copper grid covered by an amorphous carbon film. To restrict the agglomeration of the nanoparticles during drying, the copper grid was placed on a filter paper. Analytical ultracentrifugation (AUC) was performed with a Beckman Optima XL-I centrifuge (Beckman/Coulter) with a scanning absorption optics and online Rayleigh interferometer. The magnetization at applied field was measured with a commercial Quantum Design SQUID magnetometer, equipped with a 5 T superconducting magnet. The temperature dependence of the DC susceptibility was measured while cooling the sample from 300 down to 2 K in a magnetic field of 1000 Oe. For the magnetization measurements the samples were loaded into a gelatin capsule and the measurements were corrected for the diamagnetic contribution of the sample holder.