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Microwave-Assisted Nonaqueous Sol–Gel Deposition of Different Spinel Ferrites and Barium Titanate Perovskite Thin Films

Martin Kubli§, Li Luo, Idalia Bilecka, and Markus Niederberger*

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Abstract: Rapid and selective heating of solvents by microwave irradiation coupled to nonaqueous sol–gel chemistry makes it possible to simultaneously synthesize metal oxide nanoparticles within minutes and deposit them on substrates. The simple immersion of substrates, such as glass slides, in the reaction solution results after microwave heating in the deposition of homogeneous porous thin films whose thickness can be adjusted through the precursor concentration.[1] Here we use such a microwave-assisted nonaqueous sol–gel process for the formation of various spinel ferrite MFe_2O_4 (M = Fe, Co, Mn, Ni) and $BaTiO_3$ nanoparticles and their deposition as thin films. The approach offers high flexibility with respect to controlling the crystal size by adjusting the reaction time and/or temperature.[2] Based on the example of $CoFe_2O_4$ nanoparticles, we show how the crystal size can carefully be tuned from 4 to 8 nm, resulting in a continuous change of the magnetic properties.

Keywords: Microwave · Nanoparticles · Spinel ferrites · Sol–gel · Thin layers

1. Introduction

The use of nanoparticles in technological applications is strongly connected to the development of straightforward synthesis methods with minimized energy consumption and short processing times. Microwave heating is the process in which energy of electromagnetic microwaves is absorbed and converted into heat. Its volumetric nature enables rapid heating and can significantly decrease the reaction time and the energy consumption.[3] Besides accelerating reactions, another benefit emerges from the fact that the absorption is strongly material dependent. The ability to absorb microwave energy can vary by orders of magnitude among the different compounds and materials present in the reaction flask and can trigger phenomena like self-assembly.[4] Consequently, selective heating processes represent a promising alternative to conventional heating, offering new perspectives especially in the area of thin film deposition. As a matter of fact, a growing number of papers reported the microwave-assisted liquid-phase deposition of CdS,[5] indium tin oxide,[6] ZnO,[7] TiO_2,[8] $BaWO_4$,[9] or Eu:YVO4[10] on conducting glass substrates or silicon. Also core-shell nanoparticles have been prepared in the microwave by coating preformed nanoparticles with another material, *e.g.* CdTe/CdS,[11] CdSe/ZnS,[12] or Au@Ag.[13]

The nonaqueous sol–gel process for metal oxide nanoparticles is unique in its ability to be controlled on a molecular level by organic reactions.[14,15] Combined with microwave chemistry it has become a powerful tool for the preparation of highly crystalline metal oxide and phosphate particles within just a few minutes.[2,16] Such reaction systems eliminate the need for surfactants to control the particle morphology[17] and avoid post-synthetic calcination to induce crystallization. The high reproducibility and flexibility of the syntheses together with the accurate control of the microwave irradiation time, output power and thus temperature makes microwave-assisted nonaqueous sol–gel chemistry a perfect model system for the investigation of nanoparticle formation in solution. For example, zinc oxide crystallization and growth was described by combined kinetic analysis of the precursor consumption and the subsequent particle size evolution.[18] An important aspect of the study is that such a time-dependent analysis sets the basis for a precise control of particle size during heating as well as of the growth rate.

Here we present a combination of the rapid and selective microwave heating with nonaqueous sol–gel routes enabling the synthesis of uniform spinel ferrite MFe_2O_4 (M = Fe, Co, Mn, Ni) and $BaTiO_3$ nanocrystals and their simultaneous deposition as thin films. In addition to controlling the composition, the method offers the possibility to change the crystal size by simply varying the experimental parameters like temperature and time. The superparamagnetic $CoFe_2O_4$ nanoparticles, whose size could be varied from 4 to 8 nm depending on the synthesis time, showed size-dependent variation of their magnetic properties.

2. Results and Discussion

Fig. 1 provides an overview of the flexibility of the microwave-assisted nonaqueous sol–gel methodology in producing nanoparticle powders, dispersions, films and core-shell structures. $CoFe_2O_4$ nanoparticle powders, dispersions and layers can be obtained by reacting Fe(III) acetylacetonate and Co(II) acetylacetonate in benzyl alcohol (Fig. 1a–d).[1] The nanoparticles can easily be isolated as powders from the organic side products and from residual precursors by centrifugation and washing with ethanol and diethyl ether. After drying and grinding, dark brownish to black powders are obtained, whose magnetic properties are visible by naked eye upon responding to a permanent magnet (Fig. 1a). In addition to the powder, also stable dispersions

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*Correspondence: Prof. Dr. M. Niederberger
ETH Zürich
Department of Materials
Laboratory for Multifunctional Materials
Wolfgang-Pauli Strasse 10
CH-8093 Zürich
Tel.: +41 44 633 6390
Fax: +41 44 633 1545
E-mail: markus.niederberger@mat.ethz.ch

in ethanol are formed after sonicating the wet precipitate (Fig. 1b). A representative transmission electron microscopy (TEM) image shows uniform particles in the size range of 4–8 nm nicely dispersed on the TEM grid (Fig. 1c). The good dispersion of the nanoparticles is remarkable considering that no surfactants were used as stabilizers.

It is possible to deposit the ferrite nanoparticles on various substrates. For example, the immersion of glass slides in the reaction solutions results in the deposition of homogeneous films (Fig. 1d). If preformed nanoparticles are used as substrate, then it is possible to prepare core-shell structures. This approach was successfully applied in the case of Fe_3O_4 deposition on the surface of nickel nanoparticles (Fig. 1e).

The whole process can easily be extended to other metal oxides such as various ferrite spinels MFe_2O_4 ($M = Fe^{2+}$, Mn^{2+}, Ni^{2+}) and perovskite $BaTiO_3$. In the case of the ferrites, dark brownish to black powders and films (Fig. 2a) are obtained by changing the M-containing precursor. The impression that these layers are macroscopically homogeneous is confirmed by scanning electron microscopy (SEM) images. Fig. 2b and c show SEM top view images of $CoFe_2O_4$ and $NiFe_2O_4$ films, respectively. Although the layers are quite homogeneous, also a few cracks and some agglomerates attached to the surface of the films are present. However the quality of the films can considerably be improved by optimizing the washing and drying protocol after film preparation. The $BaTiO_3$ films were prepared according to a procedure described earlier for nanoparticles by reacting metallic barium with $Ti(OiPr)_4$ in benzyl alcohol.[2,19] A SEM top view image (Fig. 2d) shows homogeneous porous films similar to the ones obtained for the ferrites. Scratching the film partly off the substrate reveals an estimated layer thickness of less than 100 nm (Fig. 2e).

The crystallinity of the simultaneously formed powders was studied by X-ray diffraction. The XRD pattern in Fig. 3a corresponds to $BaTiO_3$ (ICDD PDF No. 31–174). The crystallite size extracted from the (110) reflection amounts to about 4 nm. Due to the small crystal size the reflections are too broad to discriminate between the cubic and the tetragonal structure. The pattern in Fig. 3b can be indexed to phase-pure cobalt ferrite (ICDD PDF No. 1–1121) with the inverse spinel structure.

A major advantage of the microwave-assisted liquid-phase deposition of thin films is the fact that irradiation time, temperature and precursor concentration strongly affect the particle size and the layer thickness.[1] The high potential of microwave irradiation to tailor the crystal size by varying the reaction time is confirmed by using this technique for the preparation of $CoFe_2O_4$ nanoparticles of 4.8, 6.2, 6.5

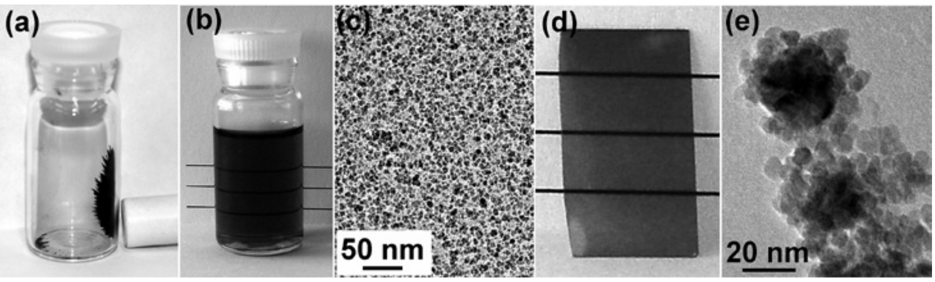

Fig. 1. a) Magnetite nanopowder under the influence of a magnet, b) $CoFe_2O_4$ dispersion in ethanol, c) TEM image of $CoFe_2O_4$ nanoparticles, d) $CoFe_2O_4$ film on a glass substrate, and e) TEM image of Fe_3O_4 nanocrystals deposited on metallic Ni.

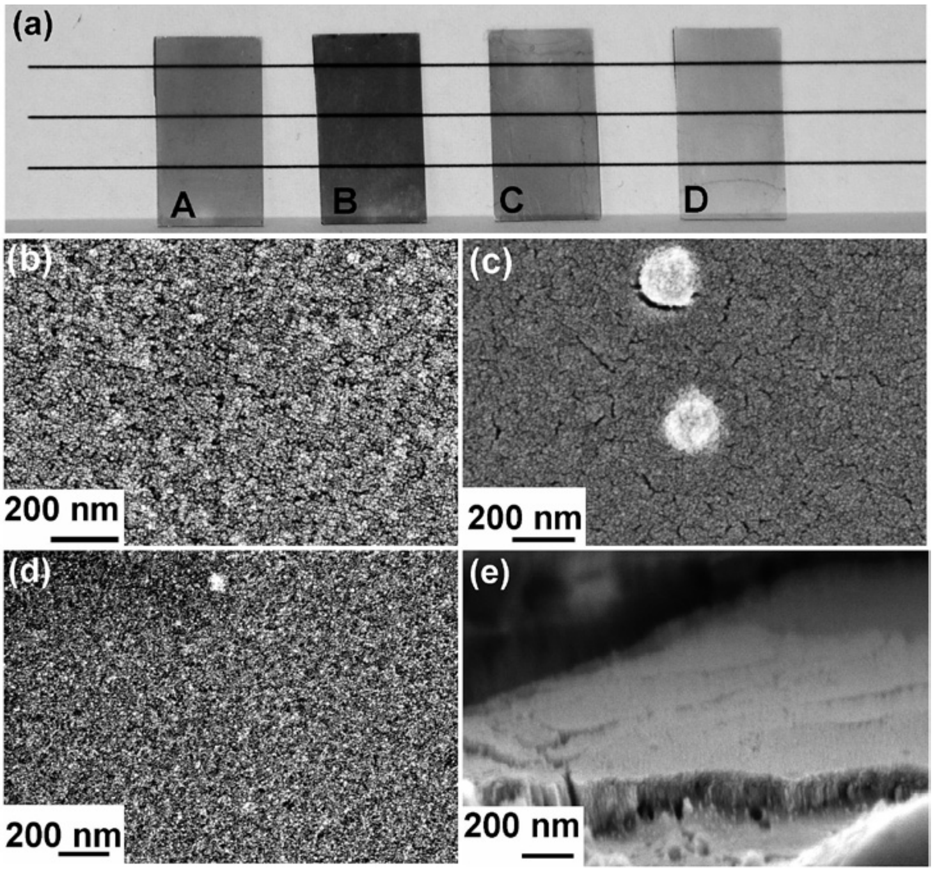

Fig. 2. a) Photograph of the ferrites films A) Fe_3O_4, B) $CoFe_2O_4$, C) $NiFe_2O_4$ and D) $MnFe_2O_4$. Top view SEM images of b) $CoFe_2O_4$, c) $NiFe_2O_4$, d) $BaTiO_3$ films, and e) side view of a $BaTiO_3$ film.

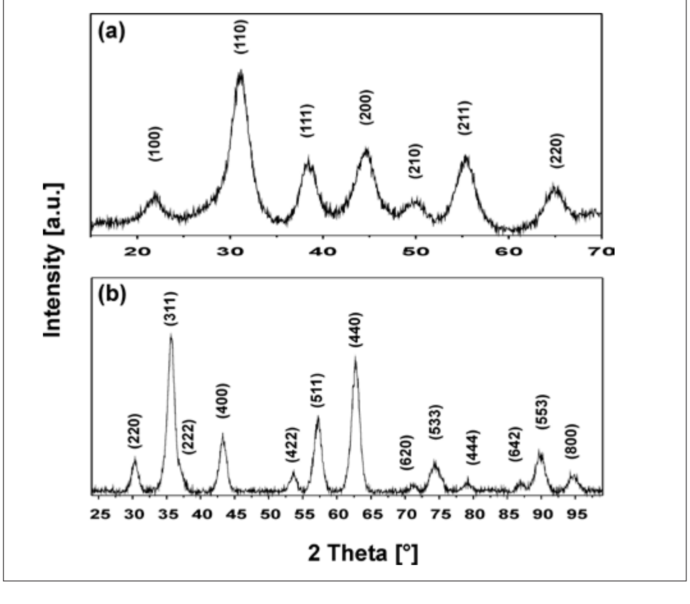

Fig. 3. X-ray diffraction patterns of a) $BaTiO_3$ and b) $CoFe_2O_4$ powders.

and 7.8 nm (average crystal size calculated from the XRD patterns). The crystal size has a strong influence on the magnetic properties. The corresponding field (FC) and zero field cooling (ZFC) magnetization curves are displayed in Fig. 4. With increasing temperature the ZFC curves reach a maximum value, *i.e.* the blocking temperature T_B. At the blocking temperature the magnetic energy barrier is equal to the thermal energy, which means that above the blocking temperature the nanoparticles do not retain any magnetization in the absence of an externally applied magnetic field and become superparamagnetic. The FC magnetization increases steadily from 300 to 2 K and deviates from the ZFC curve near the blocking temperature. The blocking temperature shifts from about 126, 141, 146 to 156 K with increased crystal size from 4–8 nm (i.e. with prolonged reaction time). Although this size dependency may be attributed to the proportionality of the anisotropy energy to the particle volume, other parameters like cation distribution, morphology, agglomeration/particle interactions and surface chemistry can also influence the blocking.[20,21]

3. Conclusion

Nanocrystalline ferrites of different composition and size can be synthesized by the microwave-assisted nonaqueous sol–gel route. The as-obtained particles exhibit superparamagnetic behavior and size-dependent coercivity. They can be deposited directly on substrates placed in the precursor solution allowing the formation of magnetic thin films. The layer deposition could also be applied to ferroelectric perovskites such as $BaTiO_3$. These results indicate that microwave-assisted nonaqueous sol–gel processes are not only a versatile tool for nanoparticle synthesis, but also for the deposition of thin films covering a broad range of compositions. After optimization of these processes it might even be possible to fabricate multilayer films, extending potential applications into the field of multiferroics.[22]

4. Experimental

4.1 *Materials*

Fe(III) acetylacetonate ≥ 99.9%, Fe(II) acetylacetonate, Co(II) acetylacetonate 97%, Ni(II) acetate tetrahydrate 99.998%, Mn(II) acetate 98%, Ba metal 99.99%, and $Ti(OiPr)_4$ 99.999% were used as precursors and anhydrous benzyl alcohol 99.8% as solvent. All chemicals were purchased from Sigma-Aldrich, stored under argon atmosphere and used as received. Glass slides 18 × 18 mm (Menzler-Gläser) were broken in half, washed in diluted HCl and sonicated.

4.2 *Synthesis of MFe_2O_4 and $BaTiO_3$ Nanoparticles*

The nanoscale transition metal ferrites and barium titanate were prepared in benzyl alcohol under similar experimental conditions as described before.[1,2,19] The ferrites were obtained by reacting 1 mmol of Fe(III) acetylacetonate with stoichiometric quantities of Mn(II) acetate, Co(II) acetylacetonate or Ni(II) acetate tetrahydrate. The precursors were transferred in a 10 ml glass tube followed by the addition of 5 ml of benzyl alcohol and microwave heating at 185 °C for 12 min. For the size-dependent studies of $CoFe_2O_4$, the irradiation time was varied from 5 to 30 min at 200 °C. In the case of $BaTiO_3$, 0.5 mmol Ba was dissolved in 5 ml benzyl alcohol at 50 °C, followed by the addition of 1 mol equivalent $Ti(OiPr)_4$ and heated for 10 min at 200 °C.

4.3 *Film Preparation*

Standard microscopy glass slides were soaked into hydrochloric acid solutions overnight, washed in deionised water and dried in air. Films were prepared by immersing the glass slides into the reaction solution containing the different precursors in benzyl alcohol. Stirring is omitted to avoid damaging of the glass slide. The samples are heated up to 185 °C, and then the temperature is maintained for 12 min.

4.4 *Instruments and Characterization*

The microwave experiments were carried out by using a CEM Discover reactor operating at a frequency of 2.45 GHz. X-ray powder diffraction studies (XRD) were performed on a Philips PW 1800 diffractometer in reflection mode using Cu K_α, $\lambda = 1.5406$ Å radiation and a post-sample monochromator. The particle size, d, was determined from the peak broadening at the (400) reflection by Scherrer's equation, $d = k\,\lambda/(\beta\cos\theta)$ where β is the peak FWHM measured in radians and θ is the Bragg angle and $k = 0.9$. The microstructure of the thin films was characterized using scanning electron microscopy (SEM, Leo 1530, Germany). The top layers of the thin films were sputtered (Bal-Tec, SCD 050, Sputter Coater) with a platinum coating to reduce any charging effects. Magnetic properties were measured using a superquantum interference design (SQUID) magnetometer MPMS 5S. Magnetic susceptibilities were measured between 2 K and 300 K in an external magnetic field of H = 1000 Oe.

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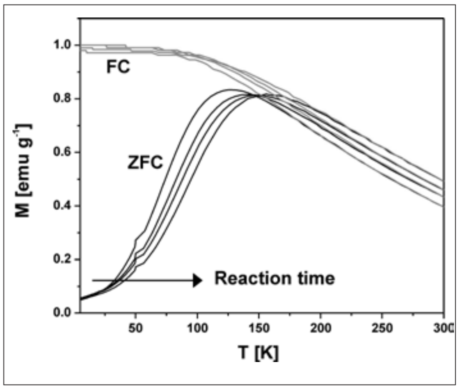

Fig. 4. Temperature dependence of the magnetization of $CoFe_2O_4$ nanoparticles obtained after 5, 12, 20 and 30 min microwave irradiation.

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