Surface Chemistry

DOI: 10.1002/ange.200602393

Efficient Preparation and Catalytic Activity of MgO(111) Nanosheets**

*Kake Zhu, Juncheng Hu, Christian Kübel, and Ryan Richards**

MgO has a typical rocksalt structure and possesses a high melting point and high ionic character. Although the stoichiometry and crystallinity are nearly constant, the morphology can vary in terms of shape, particle size, and surface structure. The MgO(100) facet is unambiguously the most stable because of its low surface energy, and it is therefore normally a product after cleavage, and it is the sole surface generated by current wet chemical methods. Numerous studies have demonstrated that the shape and size of crystalline MgO is highly influential on the adsorption properties and the configuration of the surface species formed during chemical adsorption. For example, SO_2 is found to bind in a monodentate fashion at the edge/corner sites of the aerogel nanocrystal but prefers bidentate adsorption on flat (microcrystalline) surfaces.[1,2] This selectivity is also found for acetylene in theoretical ab initio calculations and solid-state NMR experimental studies in which no stable dissociation products on the flat (100)-like surface could be obtained theoretically or experimentally.[3] Furthermore, nanostructured MgO has been reported to be extremely effective for the destructive adsorption of numerous environmental toxins and several chemical warfare agents (VX, sarin, mustard gas).[4–6] However, the (111) surface consists of alternating polar monolayers of oxygen anions and magnesium cations and thus, a strong electrostatic field perpendicular to the (111) surface is created.[7] Such a surface has provided a prototype for the study of surface structure and surface reactions, and has attracted a great geal of attention from both experimental and theoretical studies.[8,9] These studies indicate the importance of size and shape control in MgO synthesis for its applications: it is not only the surface

[*] Dr. K. Zhu,[+] Dr. J. Hu, Prof. Dr. R. Richards
International University Bremen
28759 Bremen (Germany)
Fax: (+49) 421-200-3229
E-mail: r.richards@iu-bremen.de
Dr. C. Kübel
Fraunhofer Institut für Fertigungstechnik und angewandte Materialforschung (IFAM)
Wiener Strasse 12, 28359 Bremen (Germany)
[+] Current address:
Center for Sustainable and Green Chemistry
Technical University of Denmark
2800 Lyngby (Denmark)

[**] We would like to thank the International University Bremen for financial support. K.Z. and J.H. contributed equally to this work.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

area that matters, but also the surface chemistry. Herein we report for the first time an efficient wet chemical method to synthesize MgO nanosheets that possess the (111) lattice plane as the main surface.

The MgO(111) nanosheets reported herein are likely to serve as catalysts, catalyst supports, or adsorbents with high activity and selectivity because of their unique surface chemistry. Theoretical studies on MgO(111) have suggested that the polar oxide surface may be of interest for splitting water and/or hydrogen storage.[10] When MgO(111) nanosheets were employed for the Claisen–Schmidt condensation of benzaldehyde and acetophenone, they were found to exhibit activity superior to other systems, such as $AlCl_3$, BF_3, $POCl_3$, alumina, and recently reported nanocrystalline MgO samples.[11]

The traditional method for preparing MgO is the thermal decomposition of either magnesium salts or magnesium hydroxides, which results in an inhomogeneous morphology and crystallite size as well as a low surface area. Many attempts were therefore made to tailor the texture and morphology of MgO. One of the most fruitful methods has been an adapted aerogel preparation by high-temperature supercritical drying of a toluene/methanol solvent system to yield approximately 4-nm cubic MgO polyhedron crystallites with {100} surfaces that were rich in edge and corner sites and with a surface area of 300–500 $m^2 g^{-1}$.[12–14] Furthermore, mesoporous carbon aerogels and hexagonal arrays of mesoporous carbon have been employed as hard templates for the formation of MgO during thermal decomposition of magnesium nitrate. These templates have resulted in ordered mesoporous MgO that mimic the structure of the templates and have a surface area of 150 and 306 $m^2 g^{-1}$, respectively.[15,16] Recently, a chemical vapor deposition (CVD) method was developed which produces MgO cubes with controllable particle size; however, the surface of these cubes all possess {100} surfaces and demonstrates size-dependent optical properties.[17] Preparations and studies of MgO(111) have thus far been limited to deposition on substrates such as Si(100), Ag(111), and GaAs(001),[18–20] or alternatively by mechanical polishing followed by acid etching, ion bombardment, and electron beam annealing (1000 °C) in an ultrahigh vacuum (UHV), high-temperature annealing (800 °C) in air, and also after oxygen plasma cleaning and annealing in a UHV as well as various other etching and reconstruction processes.[21–23] These studies show the diversity and complexity of MgO in terms of its shape and particle size; however, as far as surface orientation is concerned, to the best of our knowledge, neither selectivity nor controlled growth of MgO(111) has been reported for substrate-free systems.

Benzyl alcohol has been found to be a successful medium for tailoring selected metal oxides with well-controlled shapes, sizes, and crystallinity under anhydrous conditions. For example, anatase TiO_2 nanoparticles in the 4–8-nm size range,[24] vanadium oxide nanorods, and tungsten oxide nanoplatelets and nanowires with uniform morphology[25,26] were synthesized in such a medium from metal chloride precursors. We present here a simple method for preparing a sheetlike MgO with a thickness of less than 10 nm and, more interestingly, which exhibits the highly ionic (111) facet as the major surface of the "nanosheet". In our system, a mixture of water and methanol was added slowly to hydrolyze the magnesium methoxide/benzyl alcohol solution to produce the nanosheets. Theoretical studies suggest that water plays an important role: as chemisorption of water forms a hydroxy surface which stabilizes the otherwise unstable (111) surface of MgO,[27] similar interactions can occur in our system.

To synthesize these MgO(111) nanosheets, a stoichiometric amount of 4-nitro- or 4-methoxybenzyl alcohol was added to 10 wt % $Mg(OCH_3)_2$ in methanol. This was followed by the addition of a water/methanol mixture to the system and subsequent supercritical treatment and calcination in air. 4-Nitro- and 4-methoxybenzyl alcohol were chosen for their strong interaction with the inorganic intermediate $Mg(OH)(OCH_3)$, in which the hydroxy groups can interact strongly with benzyl alcohol molecules (as the latter are stronger acids than methanol), therefore, facilitating the spontaneous substitution on the interface during mixing and supercritical treatment.

The MgO nanosheets have been shown to possess the (111) plane as the main surface through a combination of bright-field transmission electron microscopy (BF-TEM), high-resolution transmission electron microscopy (HRTEM), and electron diffraction studies. BF-TEM analysis of the $Mg(OH)(OCH_3)$ precursor and the calcined MgO samples reveal that the material crystallizes with the formation of nanosheets with a typical diameter of 50–200 nm and a typical thickness of 3–5 nm (see the Supporting Information and Figure 1). The majority of the sheetlike nanoparticles are oriented almost parallel to the support film. However, some of the sheets are imaged edge on, for example, in the marked area in Figure 1.

Local energy-dispersive X-ray microanalysis (EDX) measurements on thin aggregates of the calcined MgO nanosheets on the carbon support film show that only Mg and O are present in the sample. Quantification of the Mg and O intensities reveals an Mg:O composition close to 1:2 for the sample before calcination, which is in agreement with the

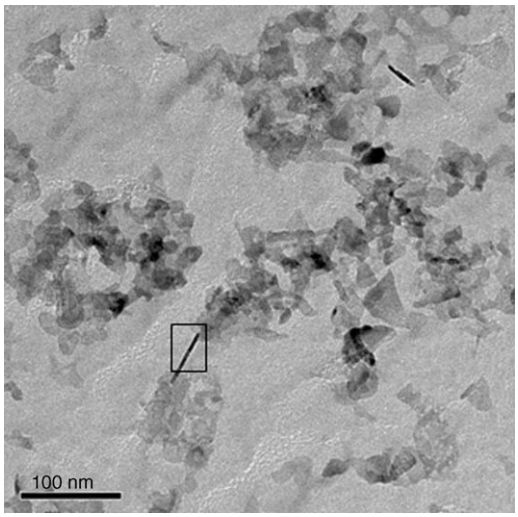

Figure 1. BF-TEM images showing larger aggregates and scattered small aggregates of MgO(111) from 4-methoxybenzyl alcohol.

formulation $Mg(OH)_2$ or $Mg(OH)(OCH_3)$. An Mg:O composition close to 1:1 has been measured for the nanosheets after calcination, which is in agreement with the formulation MgO (see the Supporting Information).

Electron diffraction studies on thin MgO aggregates proves that the MgO nanosheets crystallize in the well-known periclase structure. The observed lattice spacings are in excellent agreement with the literature *d*-spacings for periclase[28] (see the Supporting Information).

HRTEM analysis of isolated MgO nanosheets shows that their main surface is parallel to the (111) lattice planes. The MgO(111) facet is composed exclusively of oxygen in one layer and exclusively magnesium atoms in the other (Figure 2), thus, the surface of MgO(111) has a strong

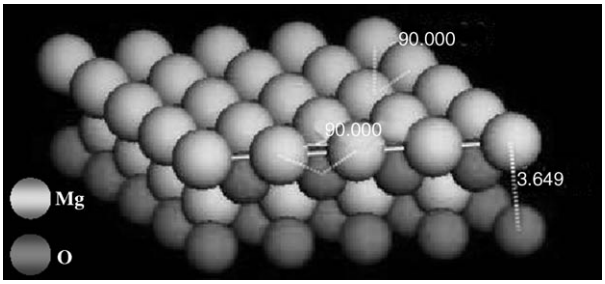

Figure 2. Illustration of the (111) facet of MgO (note the alternating layers of Mg^{2+} and O^{2-} ions).

electropolarity, either positive or negative. The HRTEM images of nanosheets viewed edge-on exhibit lattice fringes with a distance of 0.24–0.25 nm parallel to the main surface of the nanosheet, which is in good agreement with the {111} lattice spacings in MgO (Figure 3). The HRTEM images of isolated nanosheets oriented parallel to the support film typically exhibit the characteristic lattice fringes of the 111 zone, thus indicating that the sheets lie on the (111) plane, which is oriented perpendicular to the 111 zone (see the Supporting Information).

Since the addition of toluene was found to make a dramatic difference to the aerogels,[5,6] we also investigated the effect of adding toluene to our systems. TEM analysis of $Mg(OH)(OCH_3)$ nanosheets prepared with toluene added to the mixture shows similar features to those prepared without toluene. However, the nanosheets are typically larger, with a thickness of up to 25 nm and a diameter of up to 500 nm (see the Supporting Information). These larger sheets do not form uniform MgO sheets on calcination, but instead form highly porous sheets of MgO (Figure 4). Nevertheless, these porous sheets exhibit the same preference for the (111) lattice plane that forms the surface of the nanosheets (see the Supporting Information). Even though the 220, 422, and 440 reflections observed (see the Supporting Information) correspond to an almost single-crystalline domain, in most cases the crystals exhibit a rotational disorder around the [111] zone axis. Furthermore, part of the MgO is typically hydrolyzed to give rise to the weak set of {220} and {420} diffraction spots of $Mg(OH)_2$, which presumably arise from hydrolysis of the MgO nanosheets during preparation of the TEM sample. Our

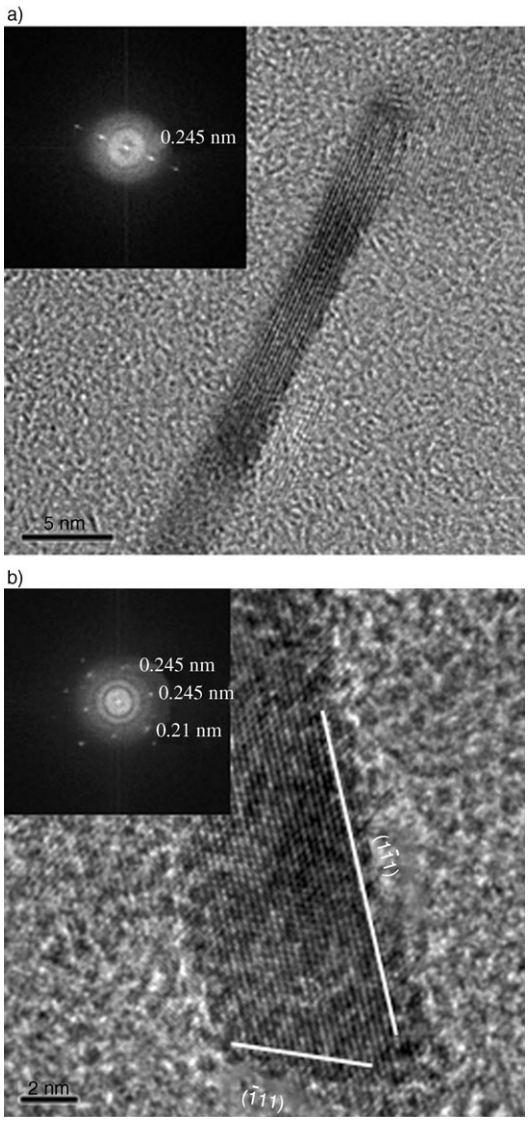

Figure 3. HRTEM images and local Fourier transforms of two isolated MgO nanosheets obtained with 4-methoxybenzyl alcohol (Figure 3 a corresponds to the marked area in Figure 1).

comparitive studies indicate that a water-free mixture does not produce MgO(111) nanosheets (see the Supporting Information).

TEM provides compelling evidence for the existence of MgO nanosheets. It seems water plays an important role in the formation of such nanosheets because a C–C bond-formation mechanism can prevail in the water-free system[29,30] instead of an acid–base interaction between the solid powder and the benzyl alcohol. Although we are still not sure of the surface species formed during the formation of $Mg(OH)(OCH_3)$, comparison of our work and that of literature studies[12–14] strongly suggest that an acid–base interaction between $Mg(OH)(OCH_3)$ and benzyl alcohol is essential for the formation of MgO nanosheets, which implies that we can tailor the preferential growth of metal oxides by careful choice of the media. As many defined oxide surfaces are a result of acid or base etching, we may use either a mild

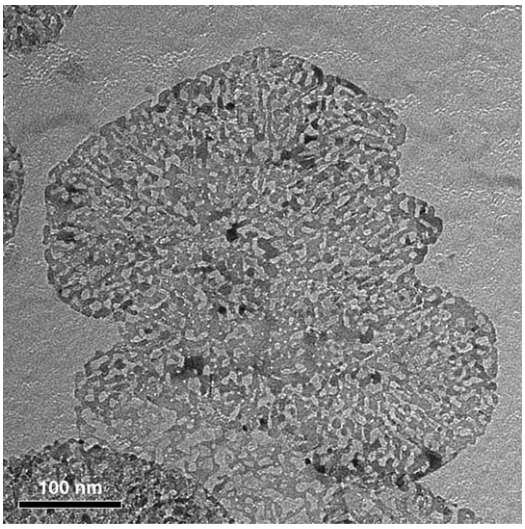

Figure 4. BF-TEM image of highly porous MgO nanosheets obtained by calcination of $Mg(OH)(OCH_3)$ nanosheets prepared in the presence of toluene and 4-methoxybenzyl alcohol.

acid or base in the precursor solution and heat the system to the supercritical phase to strengthen the acidity/basicity so that we can control the growth of a preferential surface.

It has been established for the base-catalyzed Claisen–Schmidt condensation reaction that the shape and the presence of exposed crystal facets are crucial parameters for the utilization of magnesium oxide as a solid base catalyst.[11] Polar anionic surfaces are of particular interest for the reaction, and therefore we have evaluated the catalytic activity of the MgO(111) nanosheets. Catalytic activities were determined for the Claisen–Schmidt condensation of benzaldehyde with acetophenone at 110 °C over magnesium oxide samples with different crystallites (Figure 5). CM-MgO samples are generally large cubic crystals, the NA-MgO samples are thin hexagonal platelets about 150 nm in diameter and 10 nm thick with large exposed areas of the (100) crystal facet, while the NAP-MgO samples are very small, irregular stacks of square plates with numerous crystal faces, edges, and corners. As shown in Figure 5, NAP-MgO displays higher activity in the reaction than NA-MgO and CM-MgO. This result has been attributed to the NAP-MgO possesing a single-crystallite polyhedral structure[11] which has high surface concentrations of edges and corners and various exposed crystal planes (such as (001) and (111)), hence leading to inherently high surface reactivity per unit area. It is notable that the MgO(111) nanosheets prepared from the present method display a much higher catalytic activity for the Claisen–Schmidt condensation of benzaldehyde with acetophenone than the best of the reported NAP-MgO catalysts.[11] Previous studies[11] indicate that the Claisen–Schmidt condensation is largely driven by Lewis basic O^{2-} sites, with the Bronsted basic -OH surface groups being less important in the reaction. The pronounced activity of benzaldehyde with acetophenone in the Claisen–Schmidt condensation taken together with temperature-programmed desorption studies of CO_2 (see the Supporting Information) demonstrates clearly that the MgO(111) nanosheets are Lewis basic and the MgO(111) face, which has O^{2-} ions on the surface, is particularly important for the reaction. Structure analysis based on the simulation of transmission electron micrographs has led to a proposal that structures involving oxygen trimers exist on the surface of MgO(111), thus providing a possible explanation for the excellent catalytic activity observed in the Claisen–Schmidt condensation.[9]

In summary, we have demonstrated for the first time experimentally the direct synthesis by an efficient wet chemical synthetic approach of MgO nanosheets in which (111) facets form the main surfaces. The obtained MgO nanosheets can be used as highly active solid base catalysts and may provide a prototype for the study of surface structure and surface reactions of polar oxide surfaces. The present approach may open up new simple routes to prepare well-defined crystal surfaces of metal oxides.

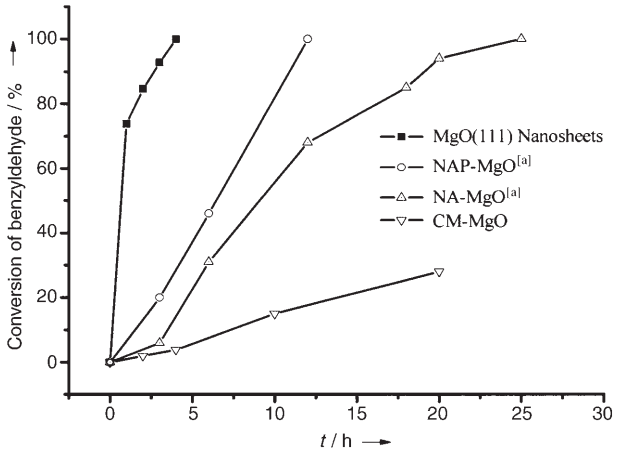

Figure 5. Claisen–Schmidt condensation of benzaldehyde with acetophenone using different crystallites of magnesium oxide at 110 °C. (NAP-MgO: aerogel-prepared MgO; NA-MgO: conventionally prepared MgO; CM-MgO: commercial MgO.) [a] From reference [11].

Experimental Section

Synthesis: In a typical synthesis of the MgO nanosheet structure (referred to here as IUB-Z-MgO), Mg belt (1.0 g) was cleaned with sandpaper and acetone. The belt was then cut into small pieces and dissolved in absolute methanol under a static argon atmosphere. After the Mg belt had totally dissolved, 4-methoxybenzyl alcohol (BZ) was added to the mixture in a Mg/BZ ratio of 2:1. After stirring the mixture for 5 h, a solution of H_2O (molar ratio of 2:1 with respect to Mg) in methanol (30.0 mL) was added dropwise with stirring. The mixture was then stirred for 12 h before being transferred to an autoclave. The autoclave containing the reaction mixture was purged with Ar for 10 min, and then a pressure of 10 bars Ar was imposed before initiation of heating. The mixture was heated at 265 °C for 15 h, and then the vapor inside vented (thereby removing the solvent in the supercritical state). A dry white powder was collected and calcined with a ramp rate of 3 °C min^{-1} to 500 °C, then maintained at 500 °C for 6 h. The ultrafine white powder produced contained solely IUB-Z-MgO, with the MgO nanoplates possessing the (111) surface on the edges.

TEM characterization of the $Mg(OH)(OCH_3)$ and MgO samples was carried out on an FEI Tecnai F20 S-Twin operated at 200 kV. The

samples were prepared by spreading an ultrasonicated suspension in ethanol on carbon-coated copper grids. TEM and high-resolution images of the nanosheets were acquired with a Gatan 794 CCD camera. Electron diffraction simulation was performed using the software MS Modeling (MS Modeling V3.0 by Accelrys).

N_2 adsorption/desorption isotherms at −196 °C were performed with a Quantachrome Autosorb 1-C system, the data were analyzed by employing the Barrett–Joyner–Halenda (BJH) method; pore volume and pore size distribution curves were obtained from the desorption branch of the isotherm.

Catalytic reactions: A mixture of acetophenone (3 mmol), benzaldehyde (2.5 mmol), and catalyst (0.175 g) was introduced into a 50-mL round-bottomed flask containing dry toluene (10 mL) and stirred in an argon atmosphere at 110 °C. Samples were taken at regular times and analyzed by GC with a flame-ionization detector. The response factors were calculated for each reactive agent from pure samples. The reaction products were identified by GC-MS.

Received: June 14, 2006
Published online: October 6, 2006

Keywords: condensation reactions · heterogeneous catalysis · magnesium oxide · nanostructures · surface chemistry

[1] E. Lucas, S. Decker, A. Khaleel, A. Seitz, S. Fultz, A. Ponce, W. Li, C. Carnes, K. J. Klabunde, *Chem. Eur. J.* **2001**, *7*, 2505.
[2] H. Itoh, S. Utampanya, J. V. Stark, K. J. Klabunde, J. R. Schulp, *Chem. Mater.* **1993**, *5*, 71.
[3] J. B. Nicholas, A. A. Kheir, T. Xu, T. R. Krawietz, J. F. Haw, *J. Am. Chem. Soc.* **1998**, *120*, 10471.
[4] J. V. Stark, D. G. Park, I. Lagadic, K. J. Klabunde, *Chem. Mater.* **1996**, *8*, 1904.
[5] J. V. Stark, K. J. Klabunde, *Chem. Mater.* **1996**, *8*, 1913.
[6] K. J. Klabunde, J. Stark, O. Koper, C. Mohs, D. G. Park, S. Decker, Y. Jiang, I. Lagadic, D. J. Zhang, *J. Phys. Chem.* **1996**, *100*, 12142.
[7] P. W. Tasker, *J. Phys. C* **1979**, *12*, 4977.
[8] J. M. Zuo, M. O'Keeffe, P. Rez, J. C. H. Spence, *Phys. Rev. Lett.* **1997**, *78*, 4777.
[9] R. Plass, K. Egan, C. Collazo-Davila, D. Grozea, E. Landree, L. D. Marks, M. Gajdardziska-Josifovska, *Phys. Rev. Lett.* **1998**, *81*, 4891.
[10] V. K. Lazarov, R. Plass, H. C. Poon, D. K. Saldin, M. Weinert, S. A. Chambers, M. Gajdardziska-Josifovska, *Phys. Rev. B* **2005**, *71*, 115434-1.
[11] B. M. Choudary, M. L. Kantam, K. V. S. Ranganath, K. Mahendar, B. Sreedhar, *J. Am. Chem. Soc.* **2004**, *126*, 3396.
[12] S. Utamapanya, K. J. Klabunde, J. R. Schlup, *Chem. Mater.* **1991**, *3*, 175.
[13] Y. Diao, W. P. Walawander, C. M. Sorensen, K. J. Klabunde, T. Rieker, *Chem. Mater.* **2002**, *14*, 362.
[14] K. T. Ranjit, K. J. Klabunde, *Chem. Mater.* **2005**, *17*, 65.
[15] W. C. Li, A. H. Lu, C. Weidenthaler, F. Schueth, *Chem. Mater.* **2004**, *16*, 5676.
[16] J. Roggenbuck, M. Tiemann, *J. Am. Chem. Soc.* **2005**, *127*, 1096.
[17] S. Stankic, M. Mueller, O Dewald, M. Sterrer, E. Knoezinger, J. Bernardi, *Angew. Chem.* **2005**, *117*, 4996; *Angew. Chem. Int. Ed.* **2005**, *44*, 4917.
[18] X. Y. Chen, K. H. Wong, C. L. Mak, X. B. Yin, M. Wang, J. M. Liu, Z. G. Liu, *J. Appl. Phys.* **2002**, *91*, 5728.
[19] R. Arita, Y. Tanida, S. Entani, M. Kiguchi, K. Saiki, H. Aoki, *Phys. Rev. B* **2004**, *69*, 235423.
[20] E. J. Tarsa, M. Degraef, D. R. Clarke, A. C. Gossard, J. S. Speck, *J. Appl. Phys.* **1993**, *73*, 3276.
[21] S. Shinozak, H. Sato, *J. Appl. Phys.* **1972**, *43*, 701.
[22] V. E. Henrich, *Surf. Sci.* **1976**, *57*, 385.
[23] V. K. Lazarov, S. A. Chambers, M. Gajdardziska-Josifovska, *Phys. Rev. Lett.* **2003**, *90*, 216108.
[24] M. Niederberger, M. H. Bartl, G. D. Stucky, *Chem. Mater.* **2002**, *14*, 4364.
[25] M. Niederberger, M. H. Bartl, G. D. Stucky, *J. Am. Chem. Soc.* **2002**, *124*, 13642.
[26] J. Polleux, A. Gurlo, N. Barsan, U. Weimar, M. Antonietti, M. Niederberger, *Angew. Chem.* **2006**, *118*, 267; *Angew. Chem. Int. Ed.* **2006**, *45*, 261.
[27] A. Wander, I. J. Besh, N. M. Harrison, *Phys. Rev. B* **2003**, *68*, 233405.
[28] S. Sasaki, K. Fujino, Y. Takeuchi, *Proc. Jpn. Acad.* **1979**, *55*, 43.
[29] M. Niederberger, N. Pinna, J. Polleux, M. Antonietti, *Angew. Chem.* **2004**, *116*, 2320; *Angew. Chem. Int. Ed.* **2004**, *43*, 2270.
[30] M. Niederberger, G. Garnweitner, N. Pinna, M. Antonietti, *J. Am. Chem. Soc.* **2004**, *126*, 9120.

