

Ordered mesoporous ZnO for gas sensing

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Abstract

We report on the synthesis and the gas-sensing properties (CO and NO₂ detection) of mesoporous zinc oxide. A two-step structure replication method for the synthesis is employed. In the first step mesoporous SBA-15 silica is prepared by the utilization of self-organization of amphiphilic organic agents. This mesoporous silica is used as the structure matrix for synthesizing mesoporous carbon CMK-3, which, in turn, is employed for yet another replication step, using zinc nitrate as the precursor. The resulting material is characterized by X-ray diffraction and nitrogen physisorption and its gas-sensing properties are compared with a non-porous ZnO sample.

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1. Introduction

It was recently shown that semiconducting mesoporous metal oxides, e.g., SnO₂ [1,2] or Co₃O₄ [3], with large specific surface areas and uniform pore widths show interesting gas-sensing properties which are superior to non-porous samples of the same metal oxides. Surface reactions on ZnO have been investigated for many years [4]. The usability of this material as a sensitive layer for resistive gas sensors has been verified [5,6]. Even though the gas-sensing properties of ZnO have been subject to research for a long time, application-specific optimization remains a challenge. A common way to tune the sensing properties is the combination of ZnO with other materials, such as CuO or SnO₂ [5]. Up to now porous ZnO materials for gas-sensing purposes have usually been prepared by conventional sol–gel techniques [6].

A well-established method to generate periodically ordered mesopore systems is the utilization of supramolecular aggregates of amphiphiles as structure-directing agents [7,8]. This approach is suitable for materials which readily form amorphous phases, such as silica and aluminosilicate [7–10], as well as aluminium phosphate [11]. However, for the majority of crystalline metal oxides, including ZnO, this concept is not

applicable [12]. This problem can be overcome by utilization of mesoporous silica or carbon phases as rigid structure matrices [13,14]. In this rather new procedure the porous matrix is impregnated with the desired precursor, which is then transformed *in situ* into the respective metal oxide. The matrix is finally removed, yielding the metal oxide as its negative replica. Using mesoporous silica as the matrix, this has yielded several new mesoporous metal oxides, including In₂O₃, Co₃O₄, Cr₂O₃, Mn_xO_y, NiO, and Fe₂O₃ [15–20]. The removal of the silica requires quite harsh chemical conditions, namely etching with hydrofluoric acid (HF) or concentrated sodium hydroxide (NaOH) solution. Accordingly, porous silica matrices are not suitable for any metal oxides which are not stable under these extreme pH conditions. Mesoporous ZnO, for example, cannot be synthesized this way, as it is soluble both at very low and very high pH. In such cases mesoporous carbon can be used as the structure matrix instead of silica, since it can be removed more gently by controlled thermal combustion. The mesoporous carbon itself is prepared by structure replication from mesoporous silica [21,22]. Thus, the entire process can be envisaged as a double replication procedure, which first yields mesoporous carbon as the negative replica of mesoporous silica, and then the mesoporous metal oxide as yet another negative replica. This has been shown to be successful for the preparation of mesoporous SiO₂ [23,24], MgO [25,26], CeO₂ [27], Al₂O₃, ZrO₂, and TiO₂ [28]. Here we present the synthesis of ordered mesoporous ZnO by utilization of mesoporous CMK-3 carbon

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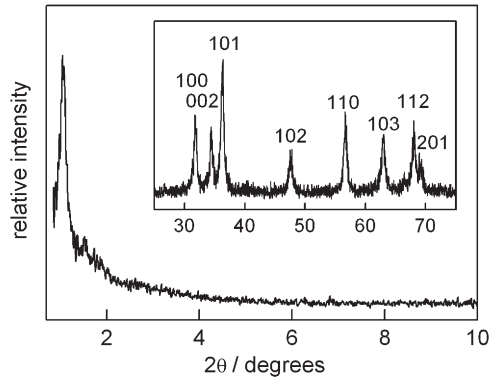


Fig. 1. XRD pattern of mesoporous ZnO. The low-angle reflections (indexes in parentheses) correspond to the periodicity of the mesopores; the wide-angle pattern confirms the crystallinity of the pore walls.

as the structure matrix. We show that the products exhibit promising properties as sensors for CO and NO₂ gases.

2. Experimental

Mesoporous SBA-15 silica was synthesized in a modification of a known literature procedure [8]. 8.5 g P-123 block copolymer (Sigma) was mixed with 325 mL HCl (1.6 mol L⁻¹) and stirred for 24 h at 308 K. After addition of 18.7 g tetraethyl orthosilicate (TEOS, Merck) the mixture was stirred at 308 K for another 24 h. The resulting gel (molar composition P-123/HCl/TEOS/H₂O=0.016/5.8/1/200) was transferred to a Teflon-lined autoclave and kept at 413 K for 24 h. The solid product was filtered off, washed with water, and calcined at 823 K for 6 h (heating rate 2 K min⁻¹). CMK-3 carbon was prepared

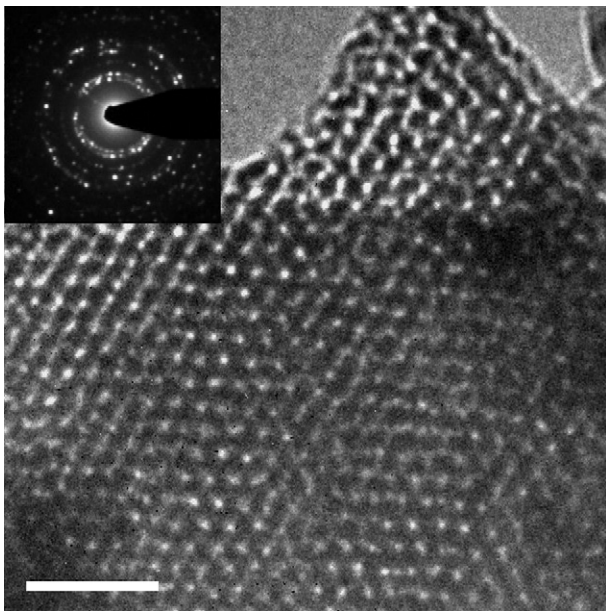


Fig. 2. TEM image of mesoporous ZnO, showing the view along the hexagonally arranged linear mesopores. The scale bar corresponds to 50 nm. The SAED pattern (insets) confirms that the material consists of small crystalline domains.

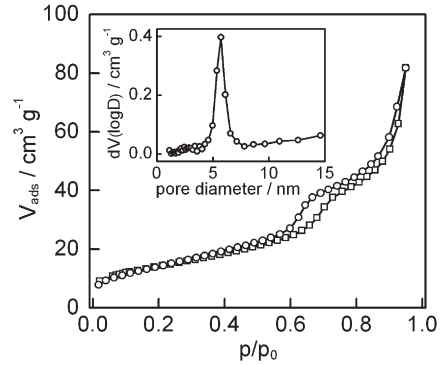


Fig. 3. Nitrogen physisorption isotherms and pore diameter distribution (inset) of mesoporous ZnO.

according to another literature procedure [21] by impregnating SBA-15 with sucrose as the carbon source, which was converted to carbon by pyrolysis in vacuum at 1173 K; the silica matrix was removed by stirring the silica/carbon sample in a 5% HF solution for 4 h at room temperature. Mesoporous ZnO was prepared by immersing 0.5 g CMK-3 carbon in 20 mL of a solution of Zn(NO₃)₂ in THF (1.5 mol L⁻¹) and stirring at room temperature for 6 h. After filtration the impregnated carbon was dried at ambient temperature, heated under air atmosphere to 573 K at a constant rate of 2.5 K min⁻¹, and kept at that temperature for 2 h to convert zinc nitrate to zinc oxide. This procedure was repeated twice. The resultant product is a powder without any specific particle morphology.

Powder X-ray diffraction was carried out on a “Bruker AXS D8 Advance” diffractometer equipped with a secondary monochromator and automatic divergence slits (filtered Cu K α radiation, 40 kV, 40 mA); the counting time was 4 s in steps of $2\theta=0.01^\circ$ for low-angle measurements ($2\theta < 10^\circ$) and 1 s in steps of $2\theta=0.02^\circ$ for wide-angle measurements ($2\theta > 10^\circ$). Nitrogen physisorption was conducted at 77 K on a Quantachrome Autosorb 6. Samples were degassed at 393 K for 24 h

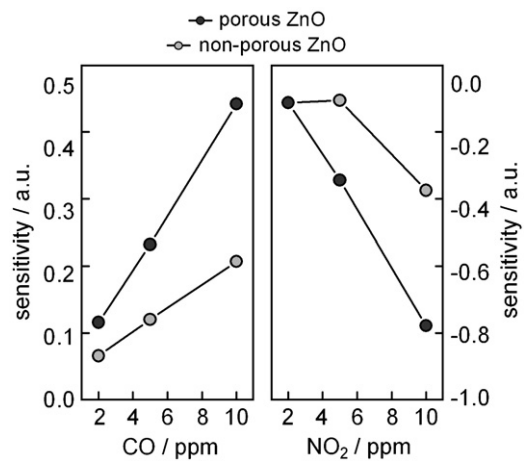


Fig. 4. Gas sensor measurements for CO and NO₂ gas at various concentrations at a relative humidity of 50% and an operating temperature of 350 °C. The dark circles show the sensitivity of the mesoporous ZnO, the light circles correspond to the non-porous ZnO sample.

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