

Functional Materials

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TEM-investigations of calcium-manganese-oxides applied for water oxidation - from amorphous state to crystalline structure

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Photosynthetic water oxidation is efficiently catalysed by a protein μ -oxido Mn_4Ca -cluster in nature [1]. This cluster consists of earth abundant, non-toxic elements and serves as a paragon for the development of synthetic calcium-manganese-oxide catalysts. In our work, the inorganic phase was synthesized in presence of an organic porogen (cyanamide), which afterwards was removed leaving behind more or less defined pores in the inorganic matrix. The microscopic structure of a series of such oxides annealed at different temperatures was characterized by transmission electron microscopy (TEM) in order to correlate crystallinity, structure on nanometer- and atomic level and surface area with catalytic activity.

(HR)TEM images and corresponding SAED pattern (Figure 1) demonstrate crystallinity (short-range order change to long-range order) combined with particle growing by increasing the calcination temperatures of the investigated calcium-manganese-oxides. Oxides, synthesized at 300°C (Figure 1a), are completely amorphous and show a rather intimate mixture between calcium-manganese-oxides and the carbon nitride precursor (Figure 1a). EDX analysis exhibits the existence of C, N, Ca and Mn. The catalytic activity of these samples is low. By annealing the oxides at 400°C, the organic phase disappears forming gaseous decomposition products and nearly pure calcium-manganese-oxides of a foam-like structure remain (Figure 1b). Nitrogen could not be observed in the EDX spectra. SAED images reveal diffuse diffraction rings with calculated d-values that belong to $Ca_2Mn_3O_8$ and $CaMn_2O_4$. That indicates the presence of disordered layered structures of edge-sharing MnO_6 octahedra with crystallites on the nanometer scale. The resulting oxides show high activity as catalysts for water oxidation. When the calcium-manganese-oxides are heated up to 550°C, the porous structure becomes denser and the pore size decreases. That may be due to the reduced amorphicity and water loss of the material resulting in structural contraction. At 700° and 1000°C, the foam- or porous structure completely disappears and instead larger crystalline particles with consequently lower specific surface areas and porosities are observed (Figure 1c). Electron diffraction experiments of different areas of that samples exhibit only the characteristic reflections of $CaMn_2O_4$ (marokite). The smaller specific surface area of the marokite crystallites yields to a decrease of the catalytic efficiency of that solid material.

Layered manganese-oxides with incorporated Ca^{2+} ions have the highest activity in catalytic water oxidation [2, 3]. In the case of the investigated calcium-manganese-oxides the high catalytic activity (sample calcined by 400°C) is due on the very small crystallites (< 5 nm) with strong structural disorder (amorphicity) at the atomic level, resulting in the high number of defect sites. The disordering providing an especially high number of both protonatable (and potentially reactive) μ_2 -O(H) bridges and terminal water coordination sites.

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3. I. Zaharieva, P. Chernev, M. Risch, K. Klingan, M. Kohlhoff, A. Fischer and H. Dau, *Energy Environ. Sci.* (2012), 5, 7081.
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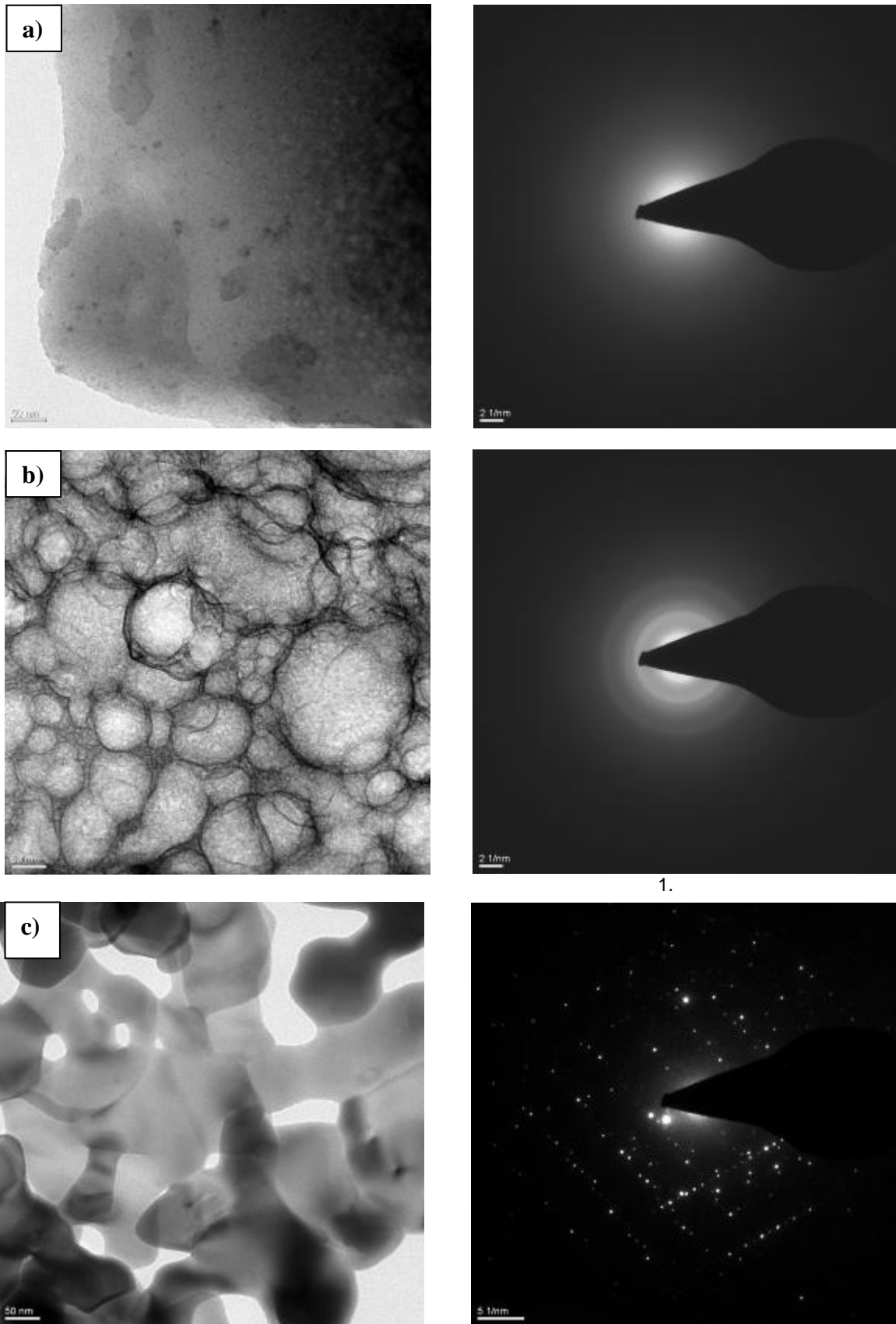


Figure 1. Bright field TEM images of calcium-manganese-oxides annealed by different temperatures and corresponding SAED pattern. **a)** 300°C, **b)** 400°C, **c)** 1000°C.