

Synthesis of Dumbbell-Shaped Manganese Oxide Nanocrystals

Xinhua Zhong,^{*,†} Renguo Xie,[‡] Litao Sun,[‡] Ingo Lieberwirth,[†] and Wolfgang Knoll^{*,†}

Max-Planck Institute for Polymer Research, 55128 Mainz, Germany, and Institute for Physical Chemistry, University of Mainz, 55099 Mainz, Germany

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Dumbbell-like homogeneous MnO nanocrystals are obtained for the first time via the pyrolysis of manganese formate in trioctylamine/oleic acid media and the orientation aggregation mechanism is proposed for this 1D growth route.

Nanocrystals have attracted great interest due to their fundamental size-dependent properties and many important technological applications.¹ The design and preparation of nanomaterials with tunable physical and chemical properties is a tremendous challenge for materials chemists. In the past decade, intensive effort has been conducted in the design and synthesis of nanocrystals with anisotropic morphologies,² because the size and shape of nanocrystals determine their physical and chemical properties. MnO is considered as a model system for the theoretical study of electronic and magnetic properties of rock salt oxides. Recent experimental results showed that MnO nanoparticles show ferromagnetic behavior, while bulk MnO displays antiferromagnetic properties.³ For this purpose, the development of a morphologically controlled synthesis of MnO nanocrystals is urgently needed to meet the demand for exploring the potentials of MnO. Anisotropic MnO nanocrystals with shapes of cube, tube, wire, branched structured, and todorokite-like are reported recently.⁴

The anisotropy of crystal structure or crystal surface reactivity was identified as the main driving force for the growth of anisotropic nanostructures. One way to obtain architectural control is to enhance anisotropic nanocrystal growth in solution media. The solution–liquid–solid (SLS) growth mechanism has been extremely successful in creating one-dimensional nanomaterials.⁵ Kotov and co-workers have demonstrated the formation of anisotropic nanocrystals by orientation alignment and recrystallization.⁶ Another common approach is to use surfactants to kinetically control the growth rates of various facets of a seed. This method has been used extensively in synthesizing many anisotropic inorganic nanocrystals.^{2,7} For the general synthetic method for metal oxide nanocrystals, the alkaline hydrolysis of metal salts in alcoholic media has been the most widely applied solution-phase chemical route, but usually with a broad size distribution.⁸ The nonaqueous synthesis of oxidic compounds started decades ago, when Gerrard et al. investigated the reaction of alcohols with silicon tetrachloride and found that hydrated silica and alkyl chlorides were formed in this reaction.⁹ More advanced processes are based on the thermal decomposi-

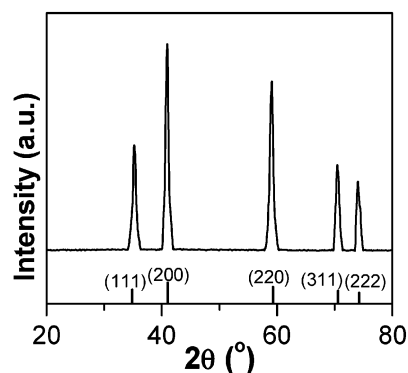


Figure 1. *p*-XRD pattern of the nanoscaled MnO dumbbells. The line XRD pattern corresponds to bulk cubic MnO (bottom).

tion of metal alkoxides or metal carboxylates in solvents such as amines or alcohols, which act as reactants as well as control agents for particle growth and architectural control, and thus allow the synthesis of high-purity monodisperse nanocrystals.¹⁰

Here, we report the synthesis and characterization of dumbbell-shaped MnO nanocrystals through the pyrolysis of manganese formate hydrate $[\text{Mn}(\text{HCO}_2)_2 \cdot x\text{H}_2\text{O}]$ in trioctylamine/oleic acid (TOA/OA) media. In a typical reaction for the synthesis, 58.0 mg (0.4 mmol) of $\text{Mn}(\text{HCO}_2)_2 \cdot x\text{H}_2\text{O}$ (from Aldrich), 0.40 mL of OA (98%, from Aldrich), and 4.0 mL of TOA (98%, from Aldrich) were loaded in a 50-mL three-necked round-bottom flask, and the mixture was degassed at 100 °C under a vacuum of ~ 1 mbar for 20 min. The reaction vessel was then filled with argon, and its temperature was increased quickly (~ 30 °C/min) to 320 °C and maintained at this temperature for 20 min under Ar flow. At 320 °C, the original clear solution turned slightly cloudy with light green color in about 7 min, which demonstrated the decomposition of the Mn precursor and the formation of MnO nanocrystals. After 20 min the solution was then cooled to ~ 50 °C. The light green solution at high-temperature turned to brown at low temperature. The formed particles were precipitated by adding methanol to the reaction mixture. The resulting organic surfactant-coated MnO particles were able to re-disperse in nonpolar solvents such as CHCl_3 or toluene and used for measurement without any size selection.

* Corresponding authors. E-mail: zhong@mpip-mainz.mpg.de; knoll@mpip-mainz.mpg.de.

[†] Max-Planck Institute for Polymer Research.

[‡] University of Mainz.

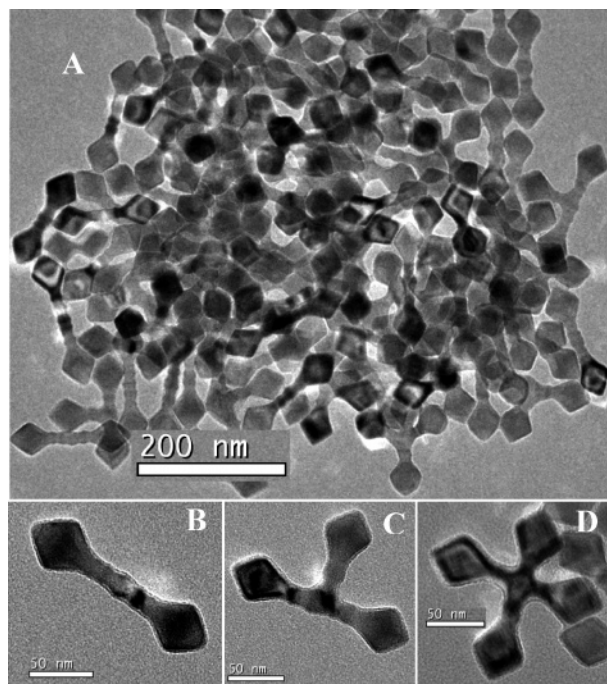


Figure 2. Low-magnification TEM images of MnO dumbbells: (A) ensemble; (B) two arms; (C) three arms; (D) four arms.

The structure and morphology of the obtained MnO nanoparticles were characterized using transmission electron microscopy (TEM, Philips EM-420 operating at an acceleration voltage of 120 kV or JEOL JEM3010 at 300 kV) and powder X-ray diffraction (*p*-XRD, Siemens D5005). TEM samples were prepared by depositing a drop of dilute toluene dispersion of nanocrystals on a carbon film coated copper grid. XRD samples were prepared by depositing nanocrystal powder on a piece of Si (100) wafer. The *p*-XRD pattern (Figure 1) reveals that the obtained MnO nanoparticles possess a cubic structure of high crystallinity. All the diffraction peaks match well with Bragg reflections of the standard and phase pure cubic rock salt structure of MnO (Fm-3m), with the measured lattice constant of this cubic phase being $a = 4.442 \text{ \AA}$.

Figure 2 shows a typical low-magnification TEM image of the prepared sample. The entire particles in the sample show dumbbell-like structure with $\sim 70\%$ of two arms, $\sim 25\%$ of three

arms, and $\sim 5\%$ of four arms. To our knowledge, the dumbbell-like morphology is the first time to be observed in inorganic nanoparticles. The dumbbells are homogeneous in size and morphology. For the two-arm dumbbells, the two arms align in a line; for the three-arm dumbbells, the three arms show a T-structure; for the four-arm dumbbells, the four arms show a “+” structure. On the end of each arm is a diamond-like arrow. The diameters of arms in all dumbbells are in the same level, with average size of around 20 nm, and the sizes of the diamond arrows in all dumbbells are also in the same level with mean size of around 35 nm in each side. The length of dumbbells is quite different. The length of two-arm dumbbells range from 150 to 210 nm, which is significantly longer than that of dumbbells with three arms (110–150 nm).

High resolution transmission electron microscopy (HRTEM) images of the dumbbells show well-defined lattice planes (Figure 3). The HRTEM images show that the lattice planes of the measured particles are perfectly aligned and the lattice planes go straight through the whole dumbbell, and the 2D lattice fringes illustrate that the nanocrystals are single crystalline with high crystallinity and confirm that the dumbbells exhibit cubic rock salt structure. The interplane spacing shown in Figure 3B is about 0.22 nm, which corresponds to the (002) plane of the cubic system of MnO. The analysis of the reciprocal lattice peaks obtained from a two-dimensional Fourier transform of the HRTEM images (Figure 3c) confirms the nanocrystals oriented along the [001] direction with its arms parallel to the [100] and [010] directions. The chemical composition of the MnO dumbbells was determined using energy-dispersive X-ray (EDX) spectroscopy analysis. In the EDX spectrum (Figure 1s in Supporting Information), the peaks of Mn and O are found and the Cu and carbon signals come from the TEM grid.

Unlike the materials with highly anisotropic crystals structures,¹¹ the 1D growth of MnO nanocrystals with their symmetric cubic lattice is unexpected. A close look at the TEM image of the arm of dumbbells (Figure 4) shows that both sides of the arm are not flat and show pearl-chain-like structure, which demonstrates trace for the aggregation of different particles. From this point we can roughly deduce that the MnO dumbbells are formed via the orientation aggregation of MnO diamond-like nanoparticles. Due to the ununiform size in the formed ensemble of MnO diamonds, the aligned arms are not flat and thus show pearl-chain-like structure. Although we cannot

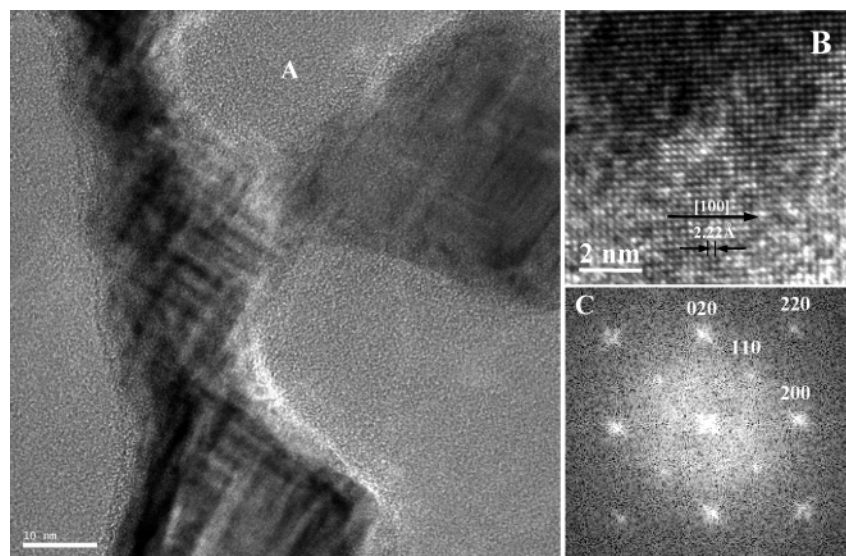


Figure 3. (A) HRTEM of a 3-arm dumbbell; (B, C) the magnification of an arrow in a dumbbell and the corresponding 2D FFT.

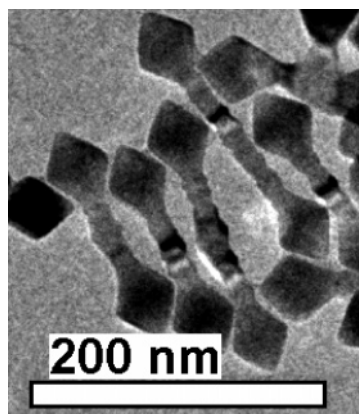


Figure 4. Pearl-chain-like structure in the arms of dumbbells.

observe the intermediate stage of this orientation assemble progress, indirect evidence supporting our proposal comes from the finding that diamond-like MnO nanocrystals can be obtained when the heating rate was decreased to 15–20 °C/min (TEM images are available in Supporting Information). Furthermore, diamond-like MnO nanocrystals were also prepared in a similar route previously.⁴ That is to say, under the set surfactant conditions, it is possible to form diamond-like MnO particles. In the second step the crystallographically specific orientation among the primary formed diamond-like MnO particles can align in different directions to form rod-, T- or +-like structures. After the completion of the aggregation, the diamond-like particles at the end of each arm grow further to form the arrows. This growth route is also observed in the formation of Au, Ag, ZnO, and CdTe 1D nanocrystals.^{6,12}

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Supporting Information Available: The EDX spectrum and the TEM image of diamond-like MnO nanocrystals. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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