Electronic Supplementary Material (ESI) for Journal of Materials Chemistry B.

Supporting Information

Intrinsic Superoxide Dismutase Activity of MnO Nanoparticles Enhances Magnetic Resonance Imaging Contrast

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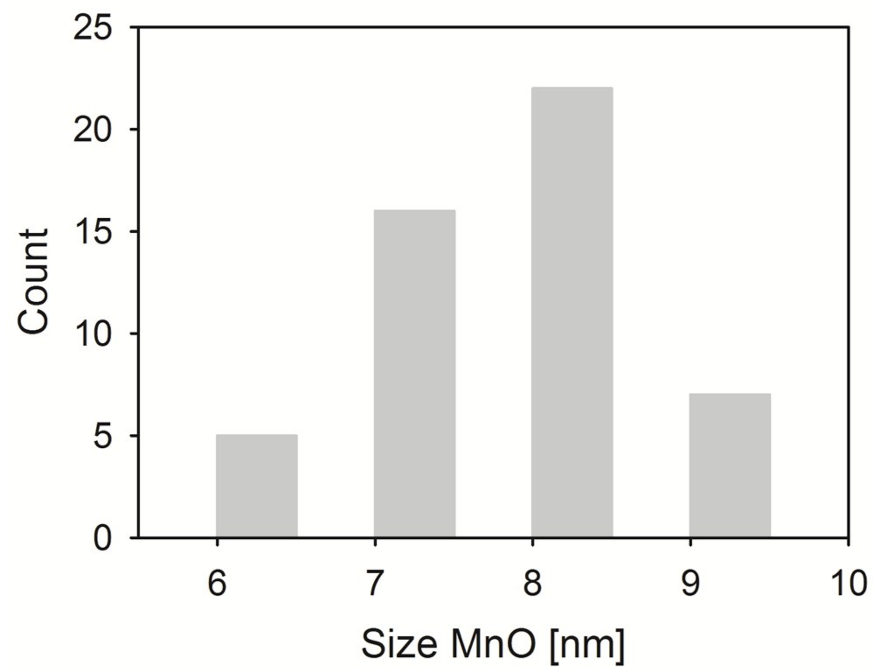

Fig. S1. Size distribution for MnO NPs determined by TEM (size of 50 individual NPs), reveiling an average diameter of 7.6±0.7 nm.

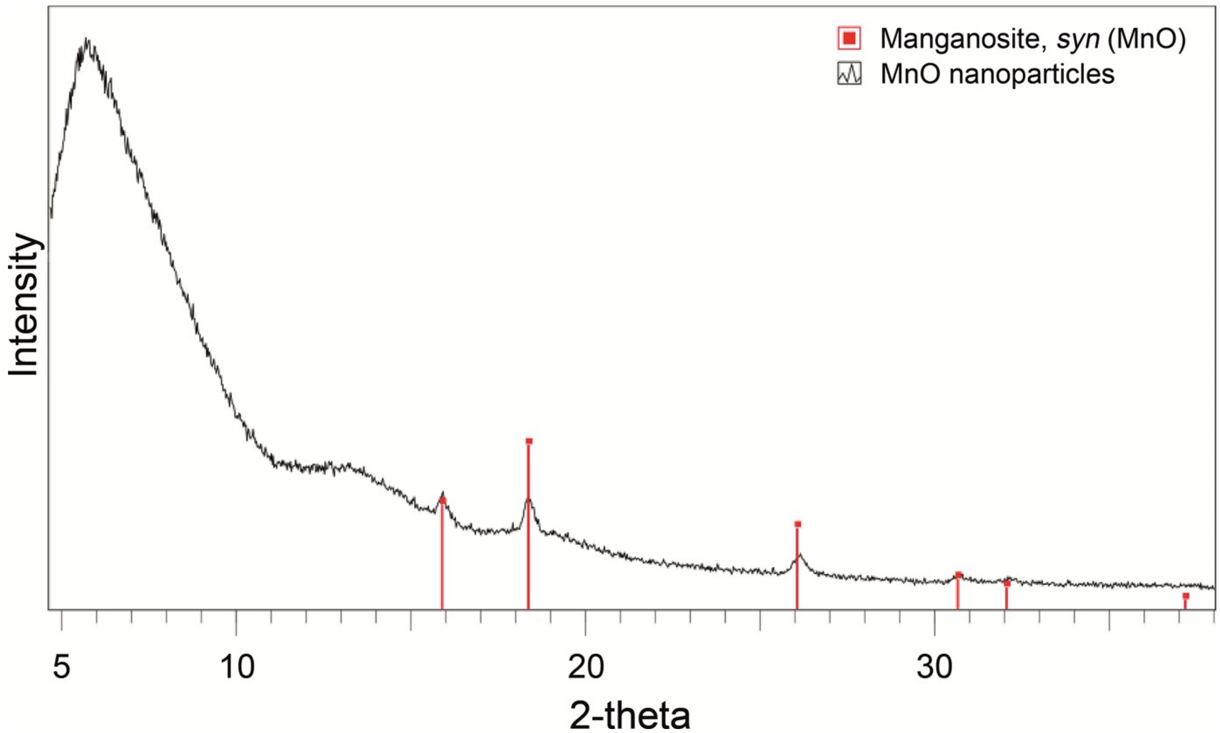

Fig. S2. P-XRD of MnO NPs (black) showing the formation of phase-pure face-centered cubic manganosite, *syn*-MnO (red).

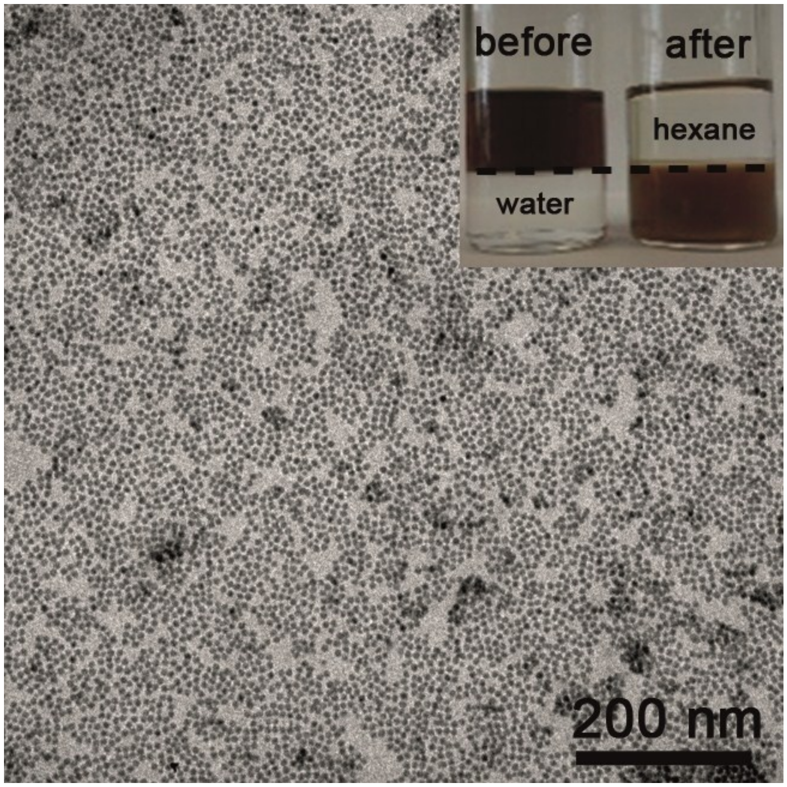

Fig. S3. Water soluble surface funcationalized 8 nm MnO NPs with C-PEG. NPs retain size and shape during the functionalization process. Scale bar: 200 nm. Inset: Phase transfer of the MnO NPs in hexane/water before (left) and after (right) the functionalization with C-PEG.

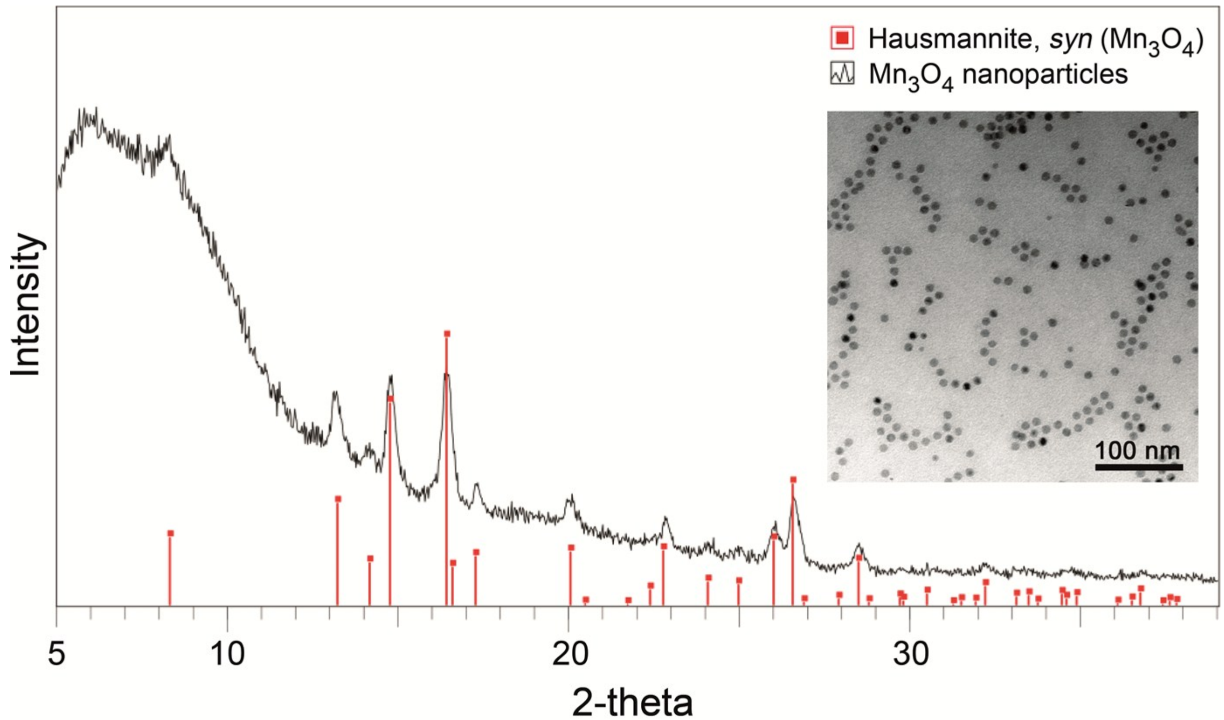

Fig. S4. Synthesis of Mn_3O_4 NPs. P-XRD of Mn_3O_4 NPs (black) showing the formation of phase-pure body-centered tetragonal hausmannite, *syn*-Mn_3O_4 (red). Inset: TEM Image of monodisperse 8 nm Mn_3O_4 NPs. Scale bar: 100 nm.

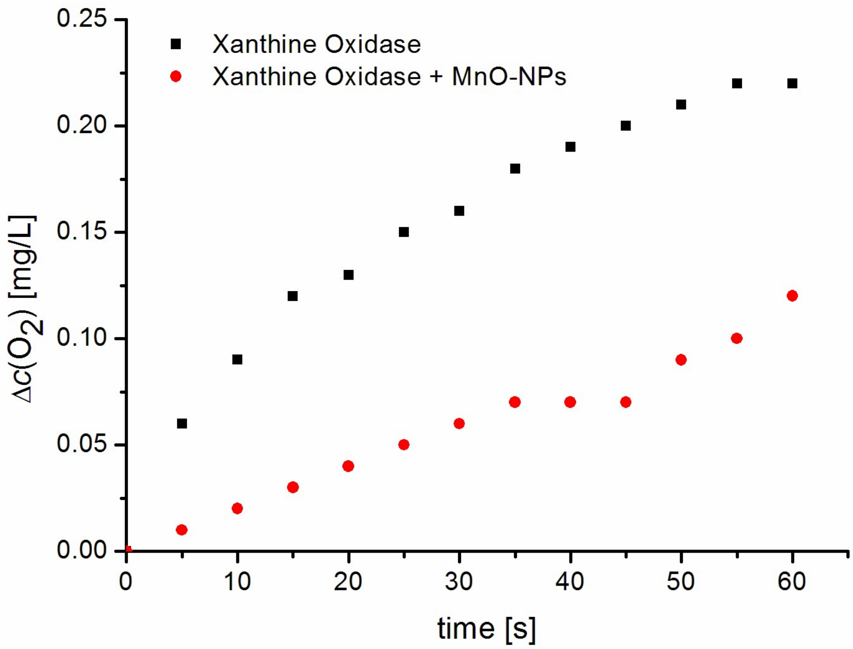

Fig. S5. Oxygen evolution of MnO NPs when exposed to superoxide radicals generated by xanthine/xanthine oxidase (XO) without addition of cytochrome c (pH 7.4). Molecular oxygen (O_2) is depleted by enzymatic activity of XO (black) forming superoxide radicals. In general superoxide dismutation by SOD-active materials leads to the formation of hydrogen peroxide and oxygen (50% each). MnO NPs reduce the oxygen depletion to approx. 50% (red), which is equivalent to the formation of an equivalent amount of O_2.

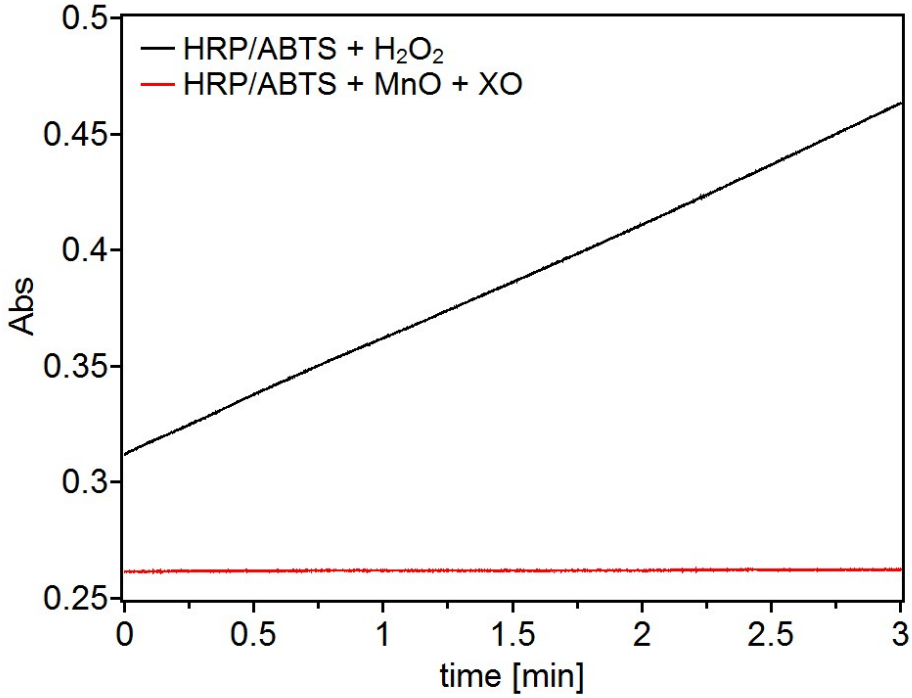

Fig. S6. Formation of H_2O_2 during the SOD-reaction of MnO NPs (red) cannot be demonstrated using the classical HRP/ABTS assay due to the intrinsic catalase-like activity of MnO NPs. As a positive control H_2O_2 has been added to the reaction mixture without addition of MnO (black).

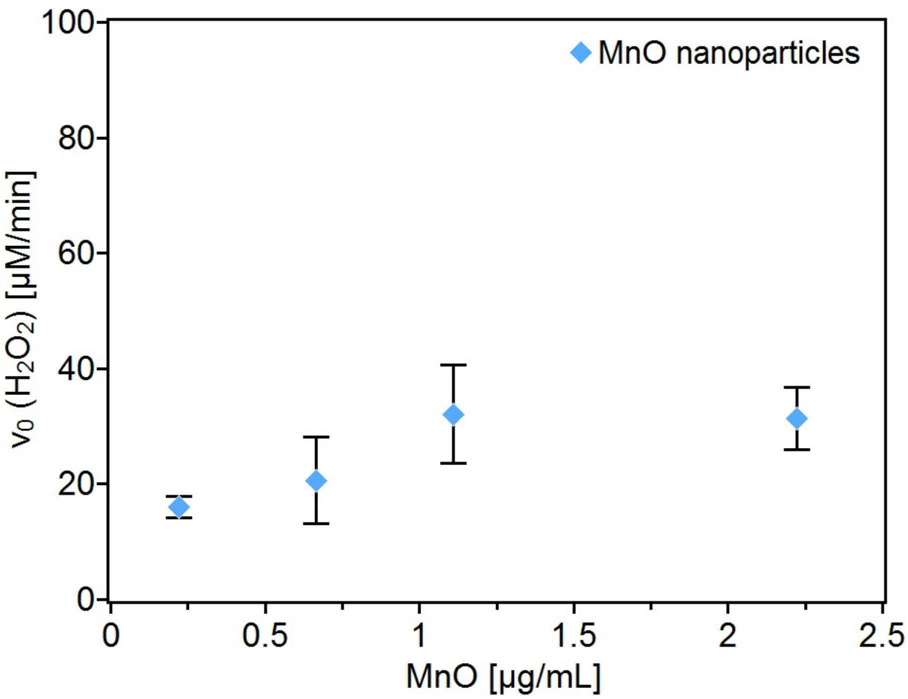

Fig. S7. Catalase-like reaction of MnO NPs monitored by disappearance of peroxide at 240 nm for 3 min at RT. Concentrations of 10mM H_2O_2 and 50 mM PBS pH 7.4 were used, while varying amounts of MnO nanoparticles (0.2, 0.7, 1.1, 2.2 µg/mL).

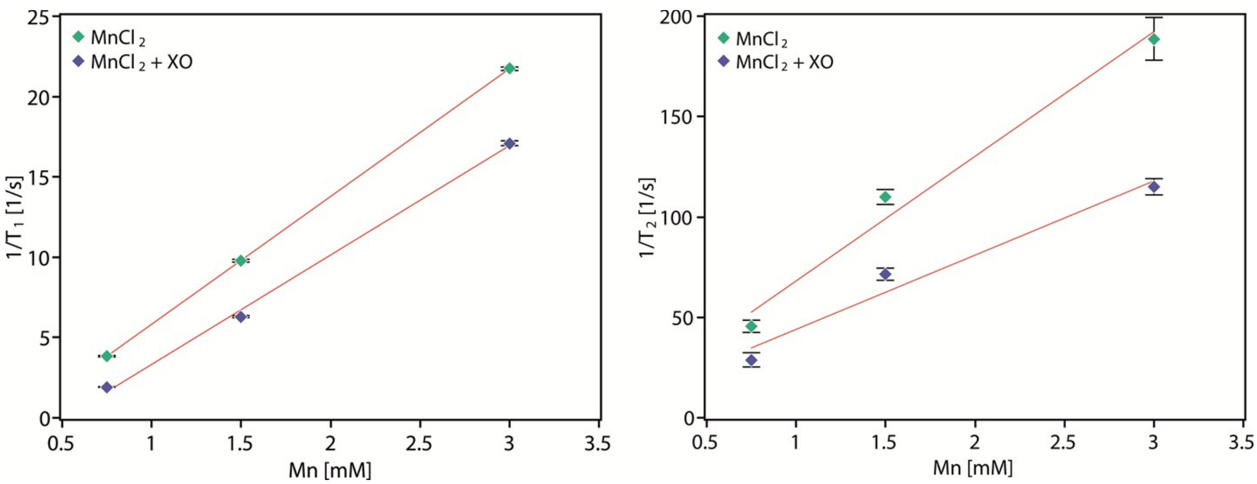

Fig. S8. Specific relaxivities r_1 and r_2 of Mn^{2+} ion a without and **b** with addition of superoxide generated by xanthine/xanthine oxidase (XO). Relaxivities were determined by linear regression and show values for **a** r_1 7.95±0.01 $mM^{-1}s^{-1}$ and r_2 62.07±8.26 $mM^{-1}s^{-1}$, **b** r_1 = 6.81±0.34 $mM^{-1}s^{-1}$ and r_2 = 36.95±6.88 $mM^{-1}s^{-1}$, respectively.

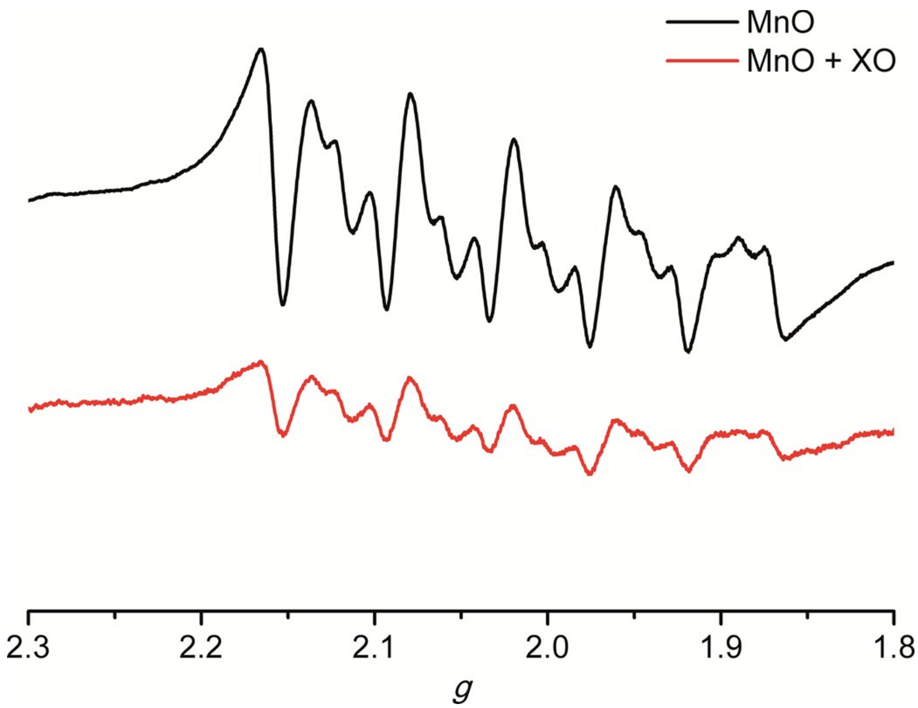

Fig. S9. X-band EPR spectra of MnO NPs in a frozen 50/50 mixture water/glycerol (77 K, 9.4 GHz) without (black) and with addition of superoxide generated by xanthine/xanthine oxidase (XO, red) after 30 min. Both spectra show the characteristic anisotropic six line pattern of Mn^{2+} (^{55}Mn; I = 5/2; 100%) with a reduction in signal intensity due to the superoxide treatment (red).