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), revealing 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 functionalized 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$_3$O$_4$ NPs. P-XRD of Mn$_3$O$_4$ NPs (black) showing the formation of phase-pure body-centered tetragonal hausmannite, syn-Mn$_3$O$_4$ (red). Inset: TEM Image of monodisperse 8 nm Mn$_3$O$_4$ 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 $\text{H}_2\text{O}_2$ 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 $\text{H}_2\text{O}_2$ 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 H₂O₂ 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 $r_1 = 7.95 \pm 0.01$ mM$^{-1}$s$^{-1}$ and $r_2 = 62.07 \pm 8.26$ mM$^{-1}$s$^{-1}$, b $r_1 = 6.81 \pm 0.34$ mM$^{-1}$s$^{-1}$ and $r_2 = 36.95 \pm 6.88$ 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).