Supporting Information

Synthesis of Magnetic Hollow Nanotubes based on the Kirkendall Effect for MR Contrast Agent and Colorimetric Hydrogen Peroxide Sensor

Mei-Yi Liao,[1] *Chih-Chia Huang,*[1] *Mong-Chen Chang,*[1] *Sheng-Feng Lin,*[1] *Tzu-Yu Liu,*[1] *Chia-Hao Su,*[2] *Chen-Sheng Yeh,*[1] *and Hong-Ping Lin*[1]*

[1]*Department of Chemistry and Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 701;* [2]*Center for Translational Research in Biomedical Science Chang Gung Memorial Hospital-Kaohsiung Medical Center Kaohsiung 833, Taiwan*

E-mail: hplin@mail.ncku.edu.tw

*Corresponding author: hplin@mail.ncku.edu.tw

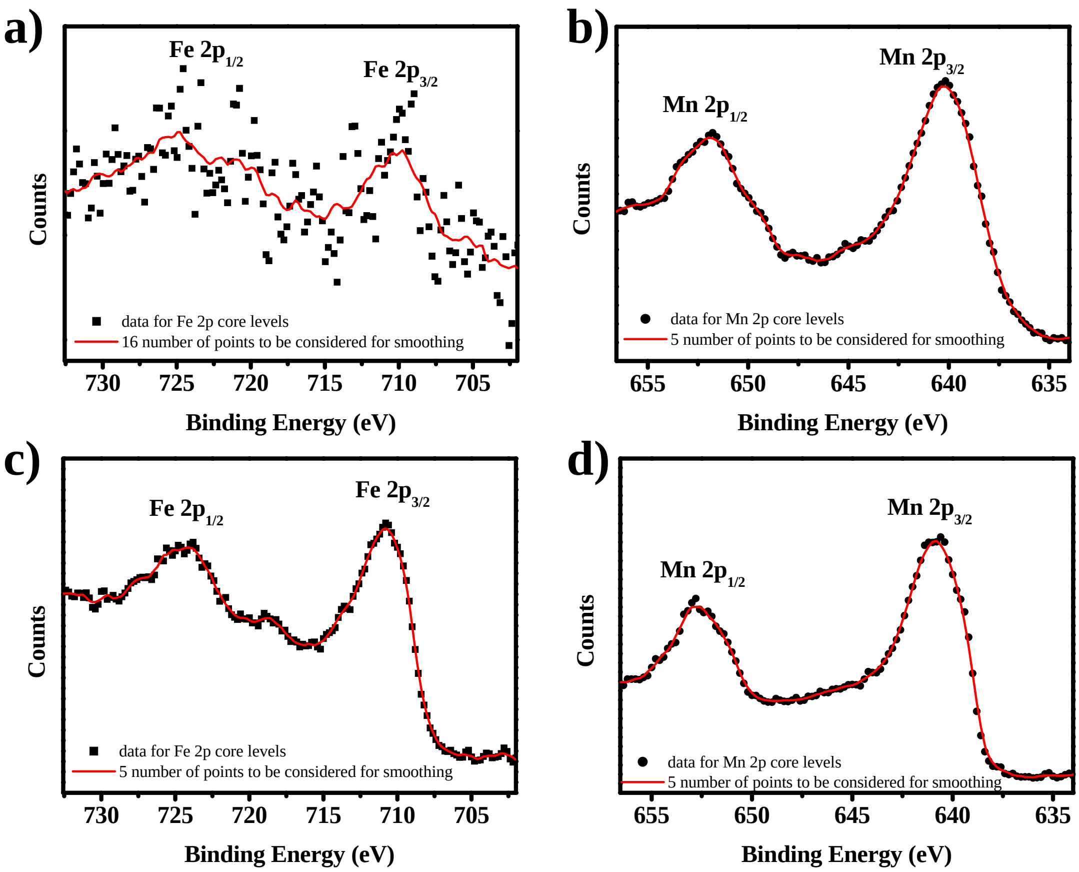

Figure S1. High-resolution XPS measurements of core-level spectra of a) Fe 2p and b) Mn 2p for $Mn_{2.5}Fe_{0.5}O_4$ nanorods and c) Fe 2p and d) Mn 2p for $Mn_{1.4}Fe_{1.6}O_4$ nanotubes.

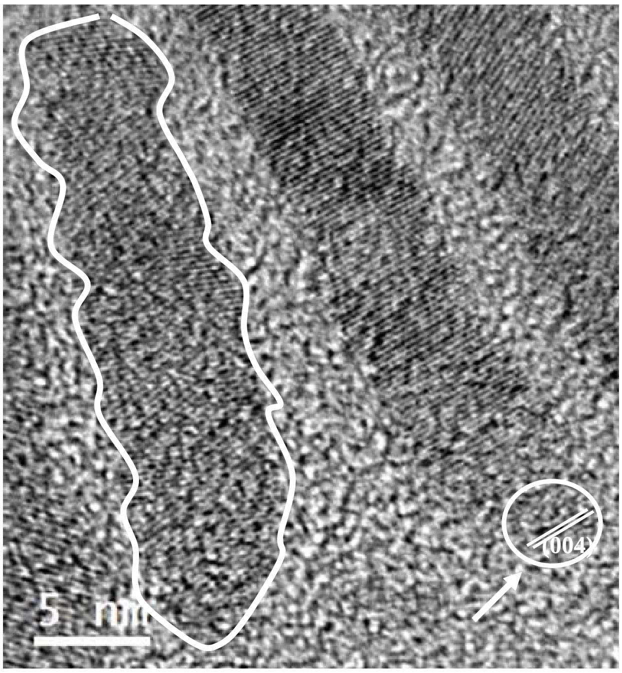

Figure S2. An HR-TEM image shows the pearl-like nanostructure of a $Mn_{2.5}Fe_{0.5}O_4$ nanorod. The area enclosed in the white line on the left contains nanocrystals. The white arrow shows a hausmannite crystallite attached to a $Mn_{2.5}Fe_{0.5}O_4$ nanorod, the lattice spacing of ~ 2.4 Å corresponds to (004) planes of Mn_3O_4 (JCPDS File 16-0154).

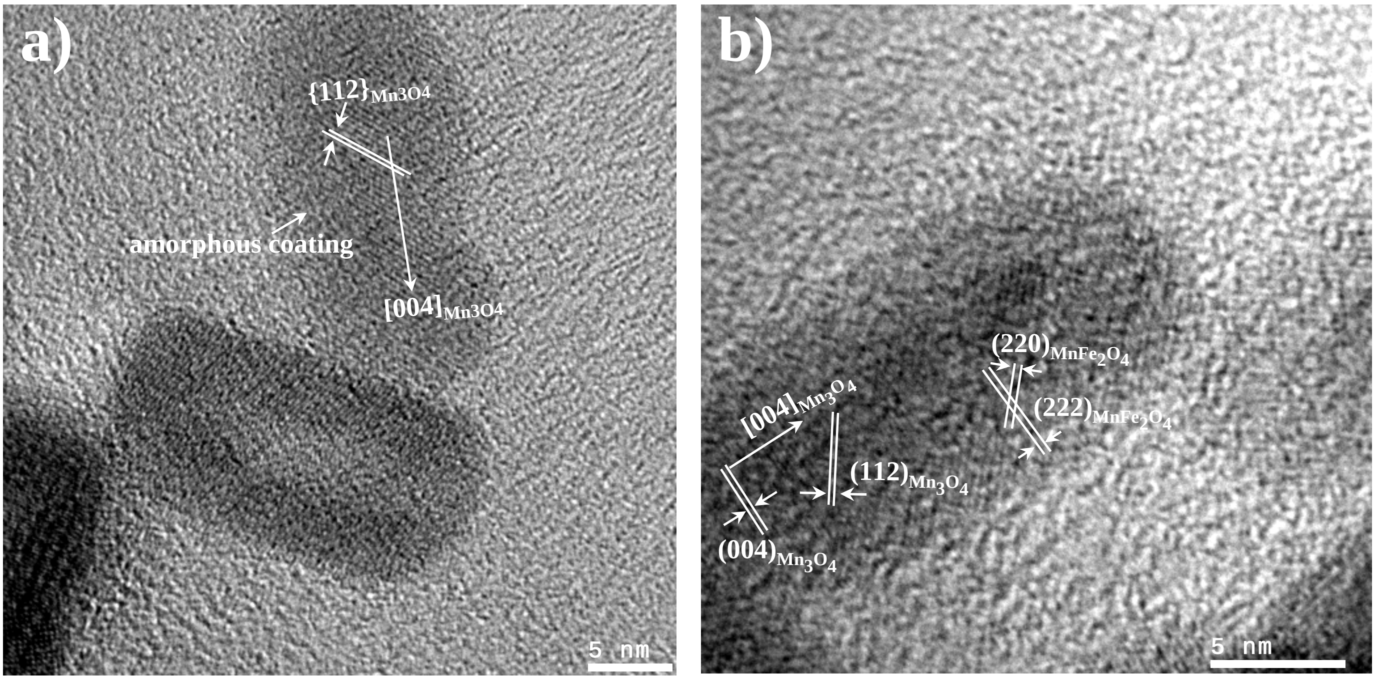

Figure S3. a) and b) **:** HRTEM images for the synthesis of Mn ferrite nanotubes after a 6-hour solvothermal reaction. The black arrow in a) shows the amorphous layer coating the [001]-grown hausmannite nanorods.

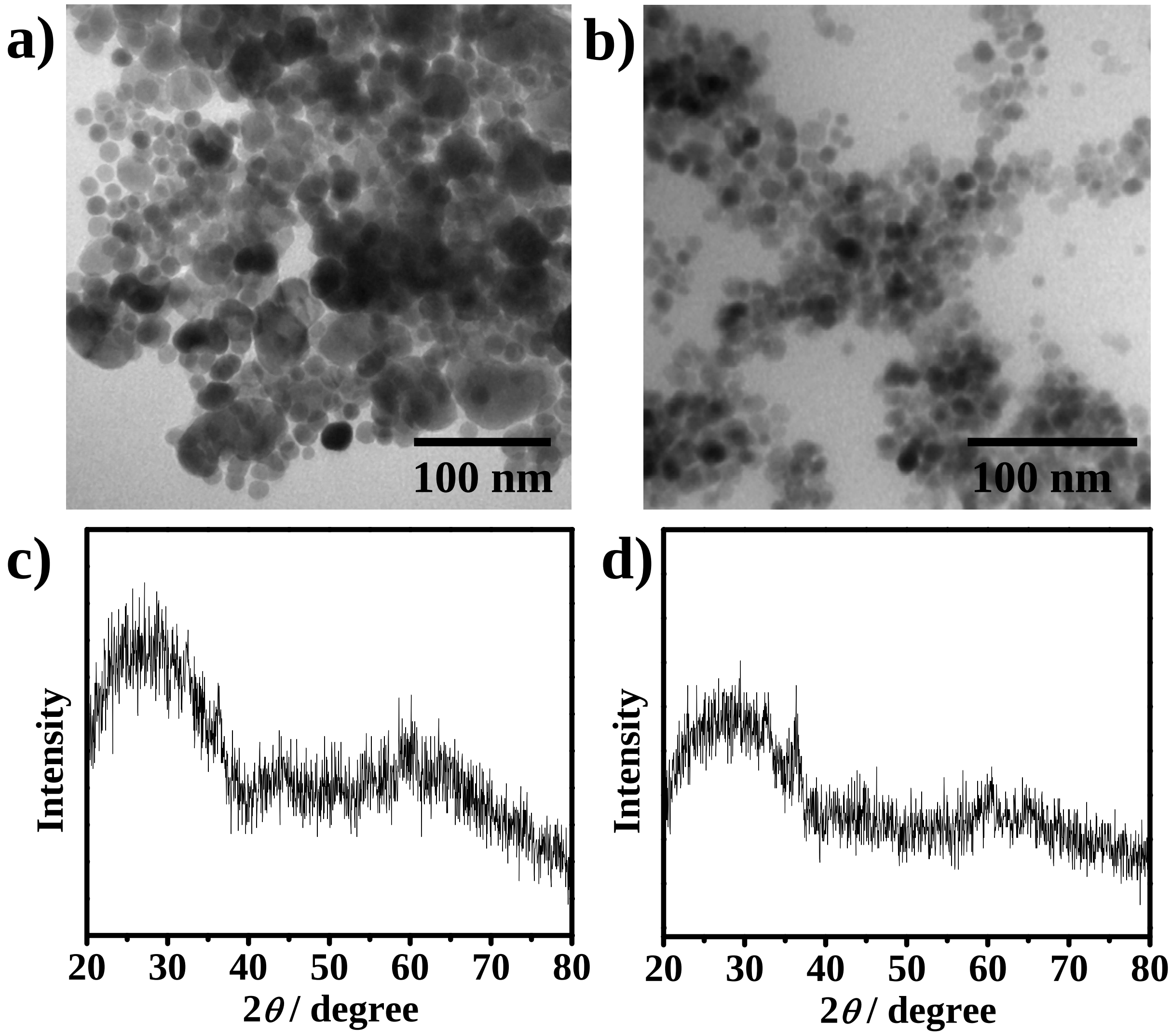

Figure S4. TEM images of a) $Fe(SA)_3$ and b) $Mn(SA)_3$ only after a 12-hour solvothermal reaction at 240 ^{o}C.

The XRD measurements from TEM images of a) and b) corresponded to those in c) and d), respectively.

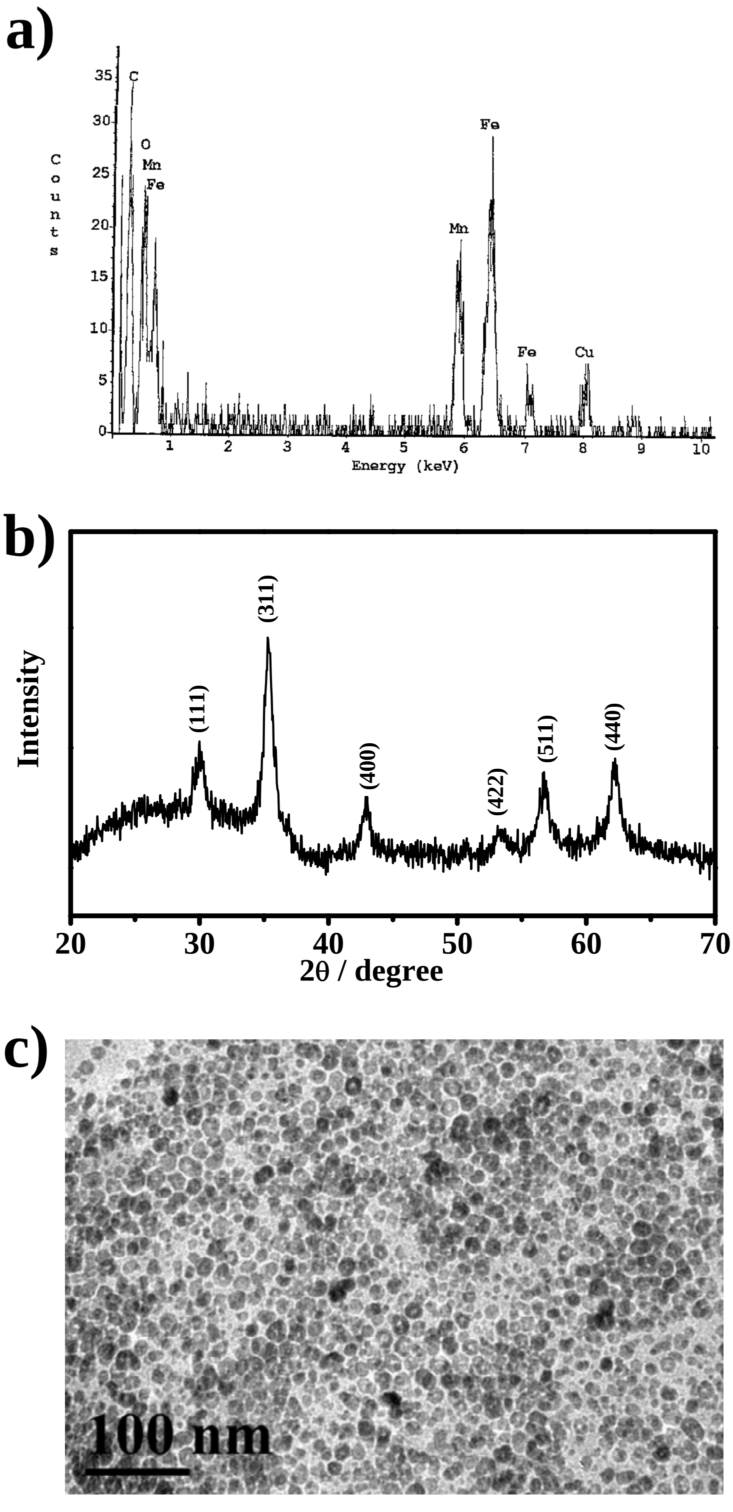

Figure S5. a) EDS analysis, **b)** XRD measurement, and c) TEM image for a 12-hour solvothermal reaction of $Fe(SA)_3$ and $Mn(SA)_2$ reacted with a $[Fe^{3+}]/[M^{2+}]$ ratio of 2: 1 in 1-octanol solvent at 240 ^{o}C.

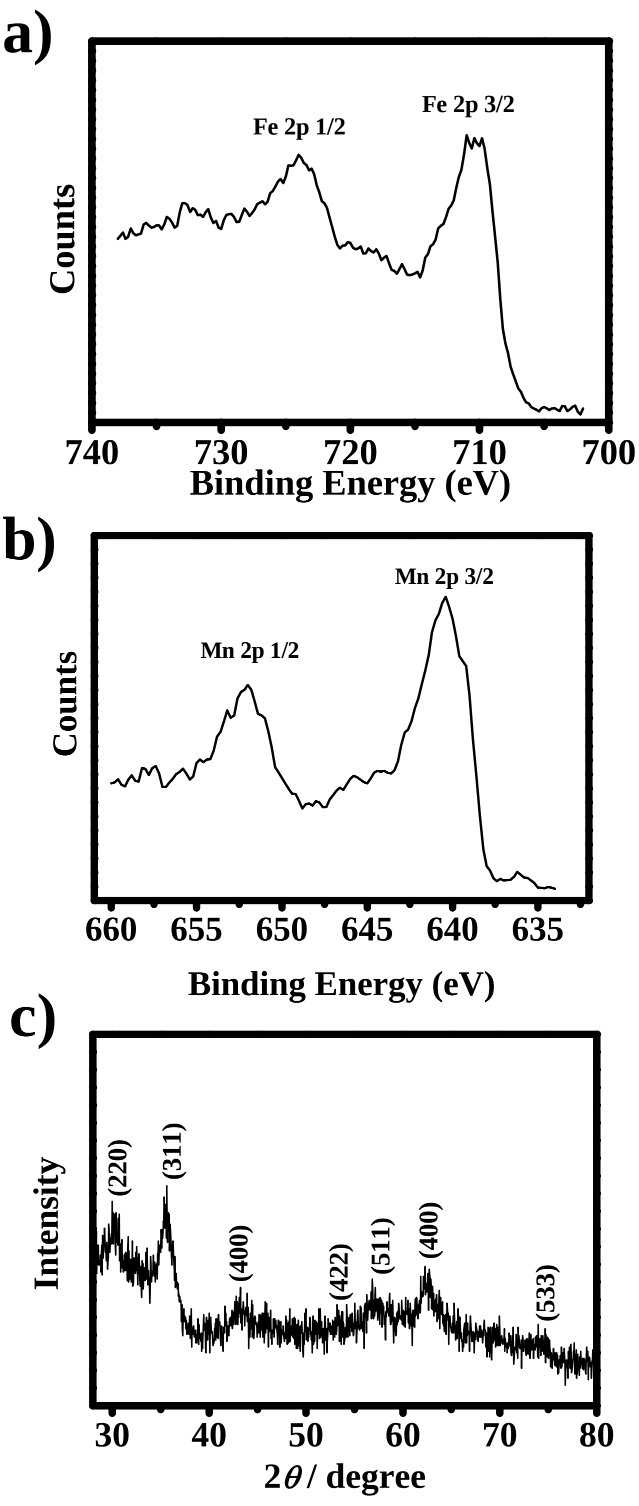

Figure S6. High-resolution XPS measurements of core-level spectra of a) Fe 2p and b) Mn 2p and c) XRD measurement for Mn_3O_4 nanoplates after a 12-hour solvothermal reaction with $Fe(SA)_3$ at 240 ^oC.

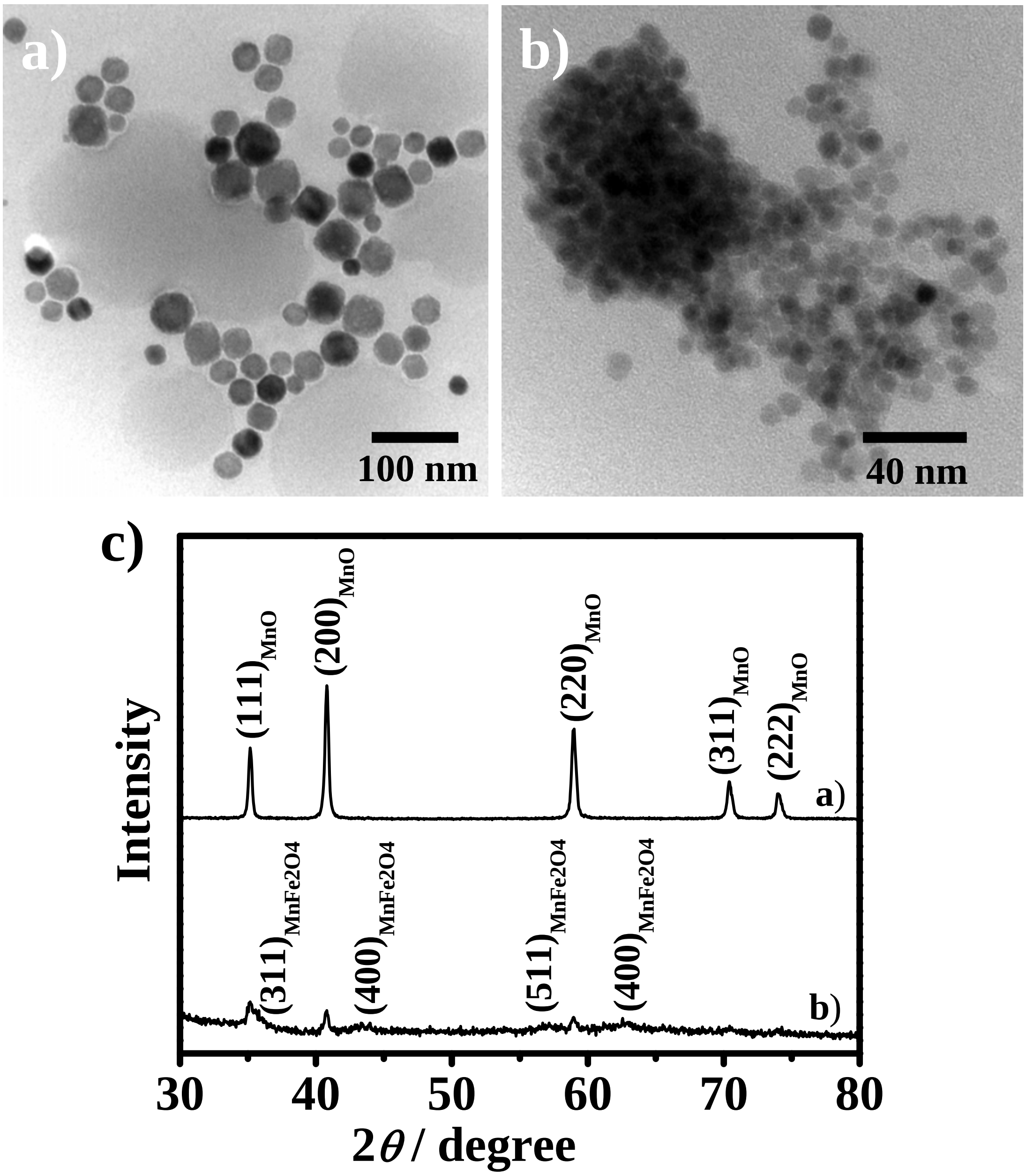

Figure S7. TEM images of a) MnO nanoparticles after a 12-hour solvothermal reaction with $Fe(SA)_3$ at 240 ^{o}C. b). The XRD measurements c) were done using the products of the TEM images in a) and b).

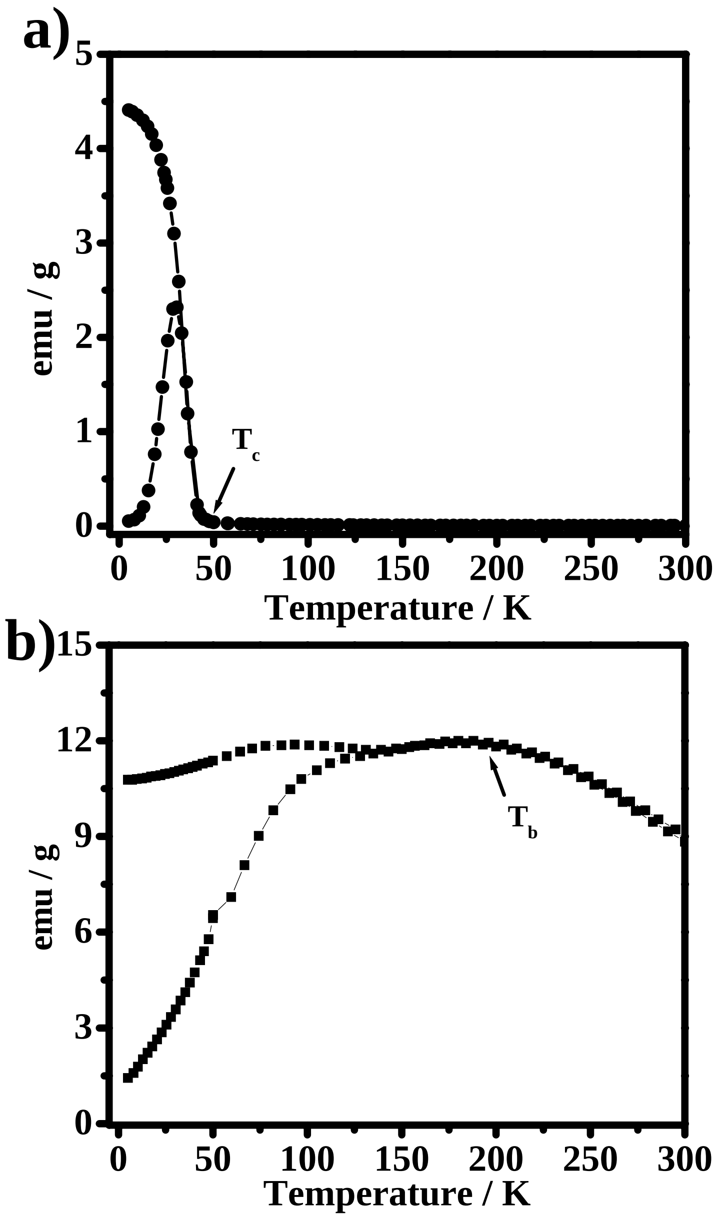

Figure S8. Zero-field-cool (ZFC) and field-cool (FC) magnetization plots in a temperature range between 5 K and 300 K under a 100-Oe field for $Mn_{2.5}Fe_{0.5}O_4$ nanorods and $Mn_{1.4}Fe_{1.6}O_4$ nanotubes, where the T_c (~ 42 K) and T_b (~ 190 K) indicate the Curie–Weiss temperatures and blocking temperatures, respectively. It has been reported that tetragonal-structured bulk Mn_3O_4[1] and nano-sized Mn_3O_4[2] exhibit ferromagnetic property at low temperature (~ 42 K), where turns into paramagnetic behavior above the T_c due to the absence of moment alignments of manganese atoms. $Mn_{2.5}Fe_{0.5}O_4$ showed a tetragonal crystal phase and may follow the magnetic behaviors as that of Mn_3O_4. For magnetic crystallites of cubic structure, when the size of nanoparticles reduced to certain size range, they exhibited a superparamagnetism at temperatures above T_b.[3] In ZFC-FC curve, that the magnetization of $Mn_{1.4}Fe_{1.6}O_4$ nanotubes decreases at temperatures above T_b indicated a superparamagnetic behavior due to the increase in thermal fluctuation.

(1) Dwight, K.; Menyuk, N. *Phys. Rev.* **1960**, *119*, 1470.

(2) Zhao, V.; Nie, W.; Liu, X.; Tian, X.; Zhang, Y.; Ji, X. *Small* **2008**, *4*, 77.

(3) Krishnan, K. M.; Pakhomov, A. B.; Bao, Y.; Blomqvist, P.; Chun, Y.; Gonzales, M.; Griffin, K.; Ji, X.; Roberts, B. *J. Mater. Sci.* **2006**, *41*, 793.

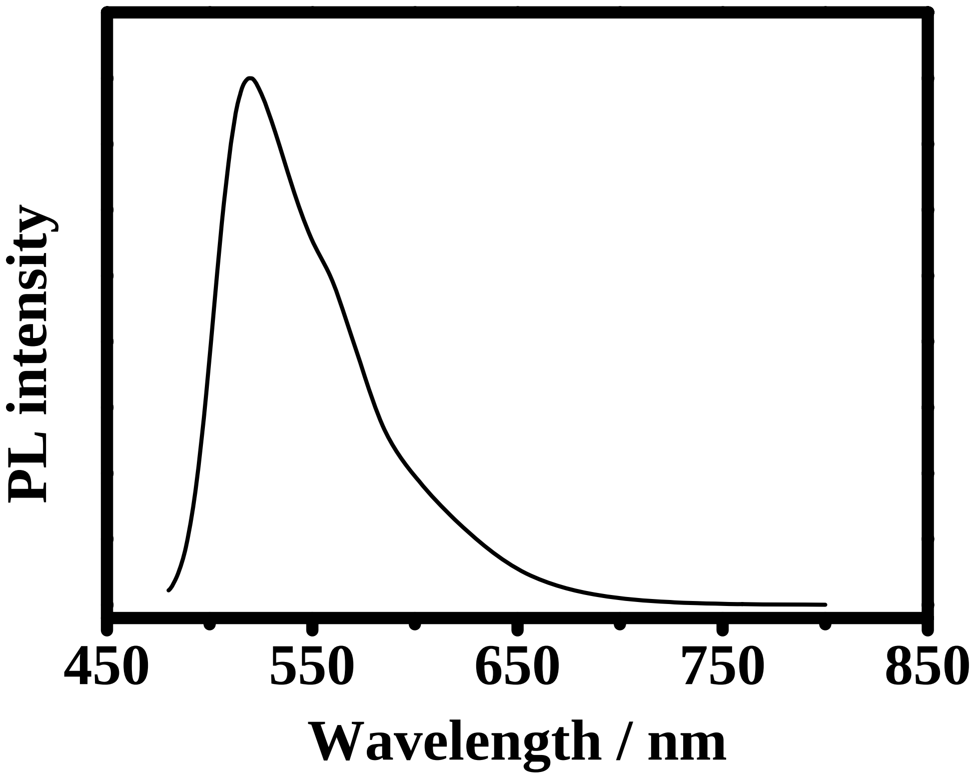

Figure S9. Fluorescence measurement for a $Mn_{1.4}Fe_{1.6}O_4$@PAH nanotube conjugated with fluorescein isothiocyanate (FITC).

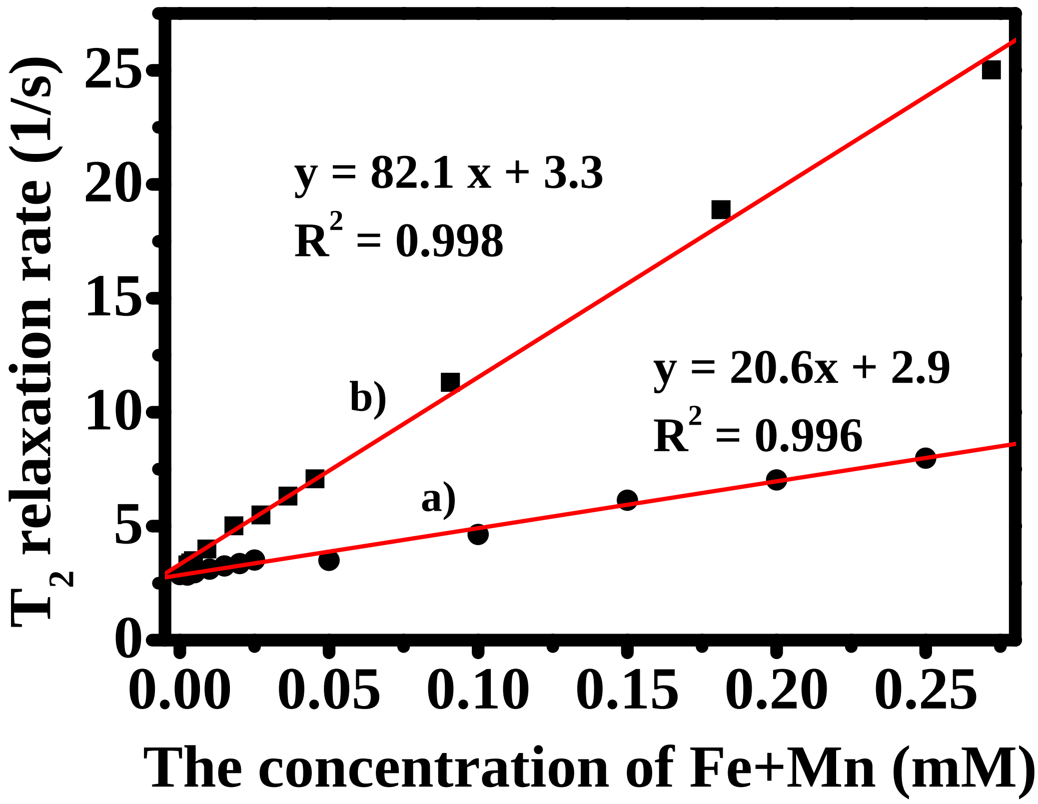

Figure S10. T_2 relaxation ($1/T_2$, s^{-1} (black curve)) rates of a) $Mn_{2.5}Fe_{0.5}O_4$@PAH nanorods and b) $Mn_{1.4}Fe_{1.6}O_4$@PAH nanotubes.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry

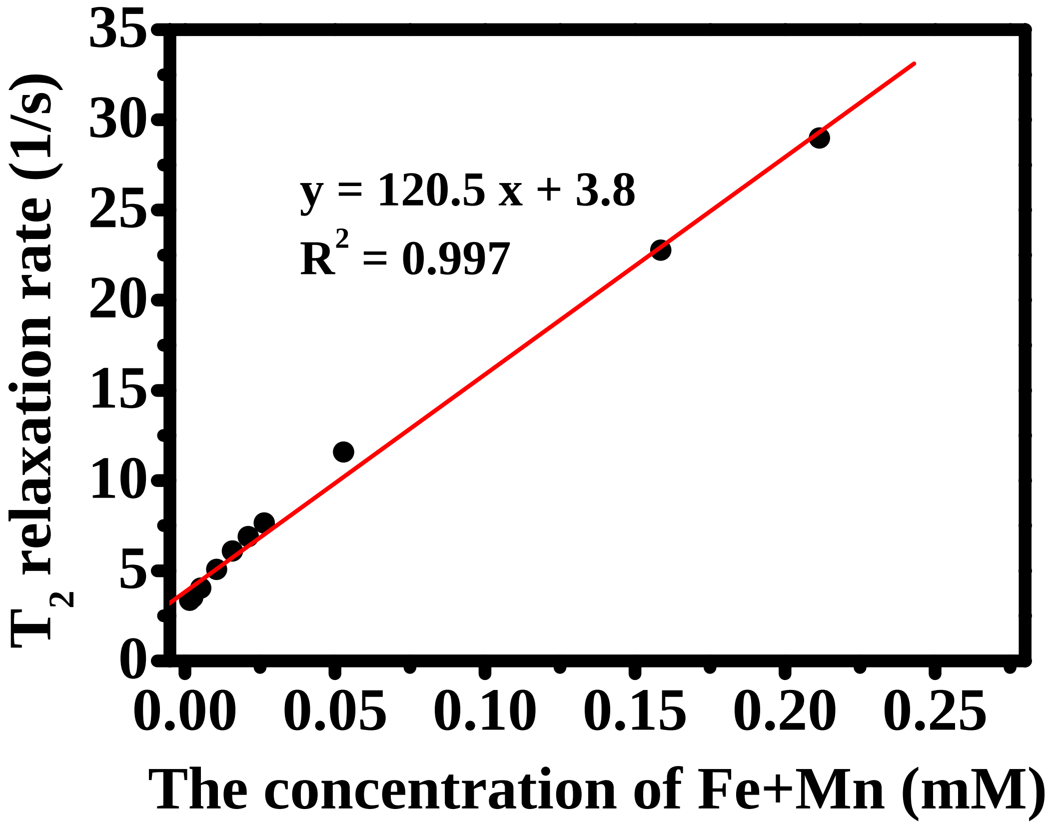

Figure S11. T_2 relaxation ($1/T_2$, s^{-1} (black curve)) rates of hollow $MnFe_2O_4$ nanoparticles from a 12-hour solvothermal reaction of Mn_3O_4 nanoplates and $Fe(SA)_3$ at 240 °C.

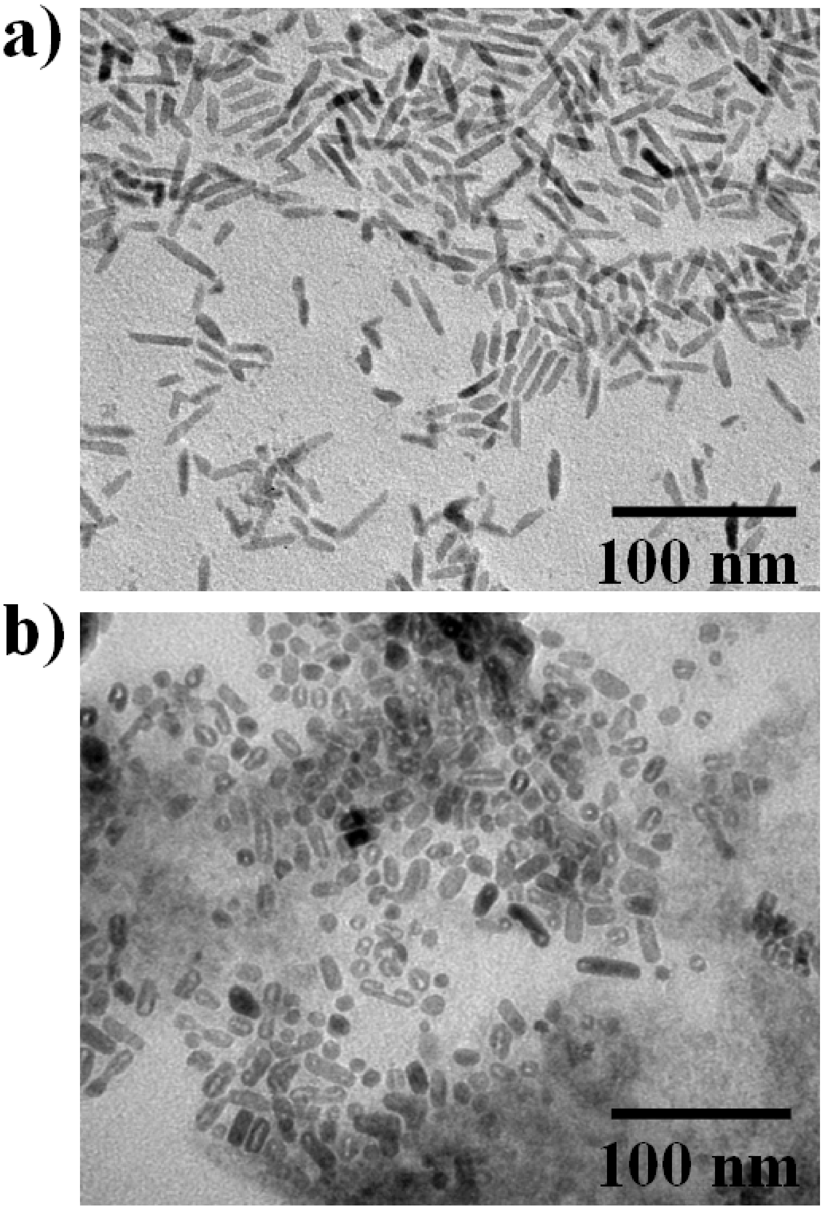

Figure S12. TEM images of $Mn_{2.5}Fe_{0.5}O_4$ nanorods a) and $Mn_{1.4}Fe_{1.6}O_4$ nanotubes b) determined after heterogeneous catalysis.