

Support Information

A very simple method to synthesize nano-sized manganese oxide: An efficient catalyst for water oxidation and epoxidation of olefins

Mohammad Mahdi Najafpour^{*1,2}, Fahimeh Rahimi¹, Mojtaba Amini^{*3}, Sara Nayeri¹ and Mojtaba Bagherzadeh⁴

¹ *Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanzan, 45137-66731, Iran*

² *Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanzan, 45137-66731, Iran*

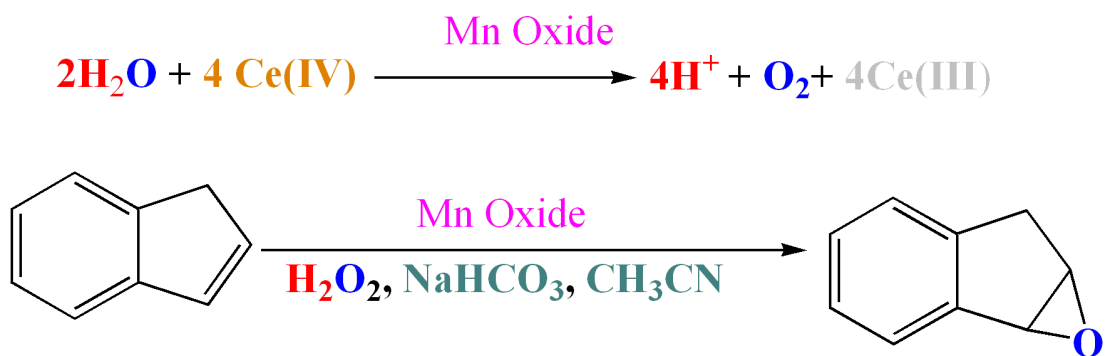
³ *Department of Chemistry, Faculty of Science, University of Maragheh, Golshahr, P.O. Box: 55181-83111731, Maragheh, Iran*

⁴ *Chemistry Department, Sharif University of Technology, PO Box 11155-3516, Tehran, Iran*

Corresponding authors; Phone: (+98) 241 415 3201; E-mail:

mmnajafpour@iasbs.ac.ir (MMN); Phone: (+98) 421 2278900; E-mail:

mamini@maragheh.ac.ir (MA).



Scheme S1. Chemical equations for the studied reactions.

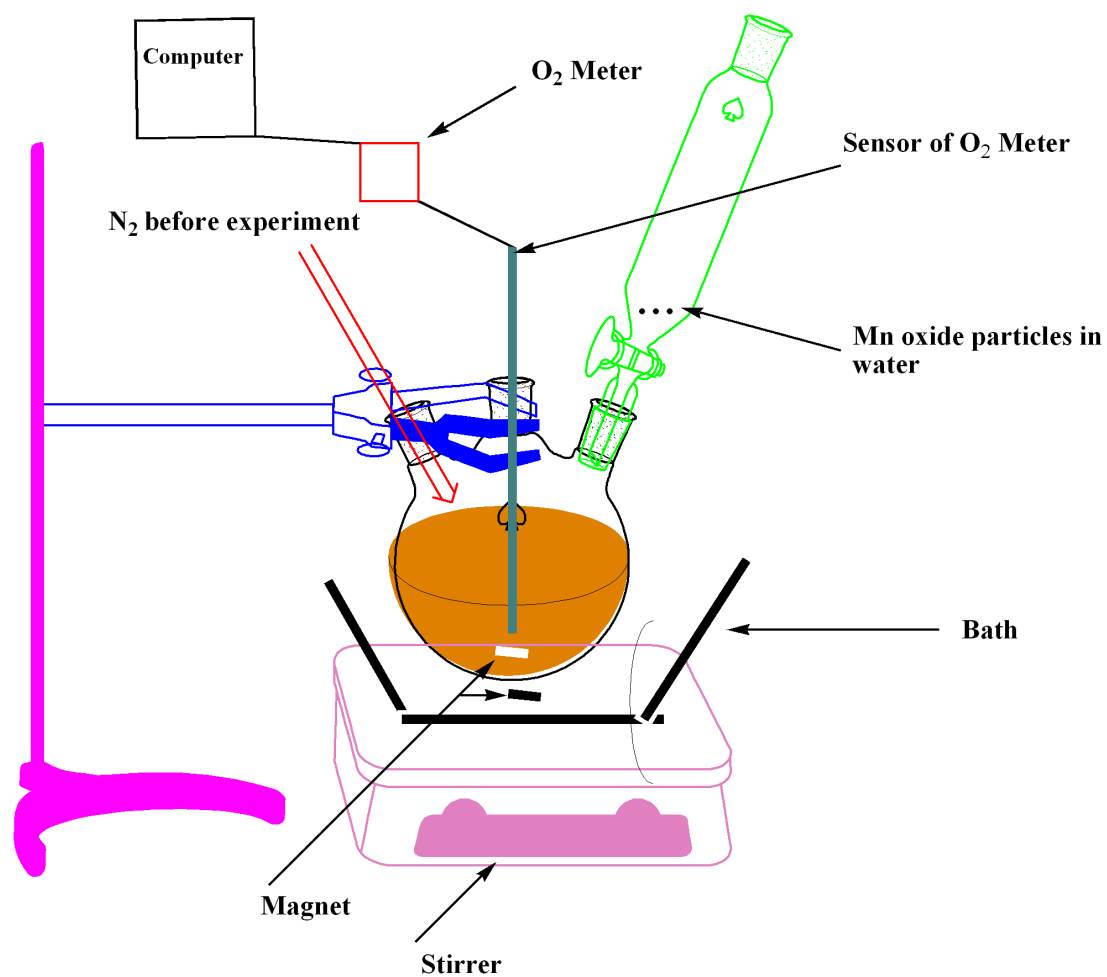


Fig. S1. The reactor set-up for oxygen evolution experiment in the presence of Ce(IV).

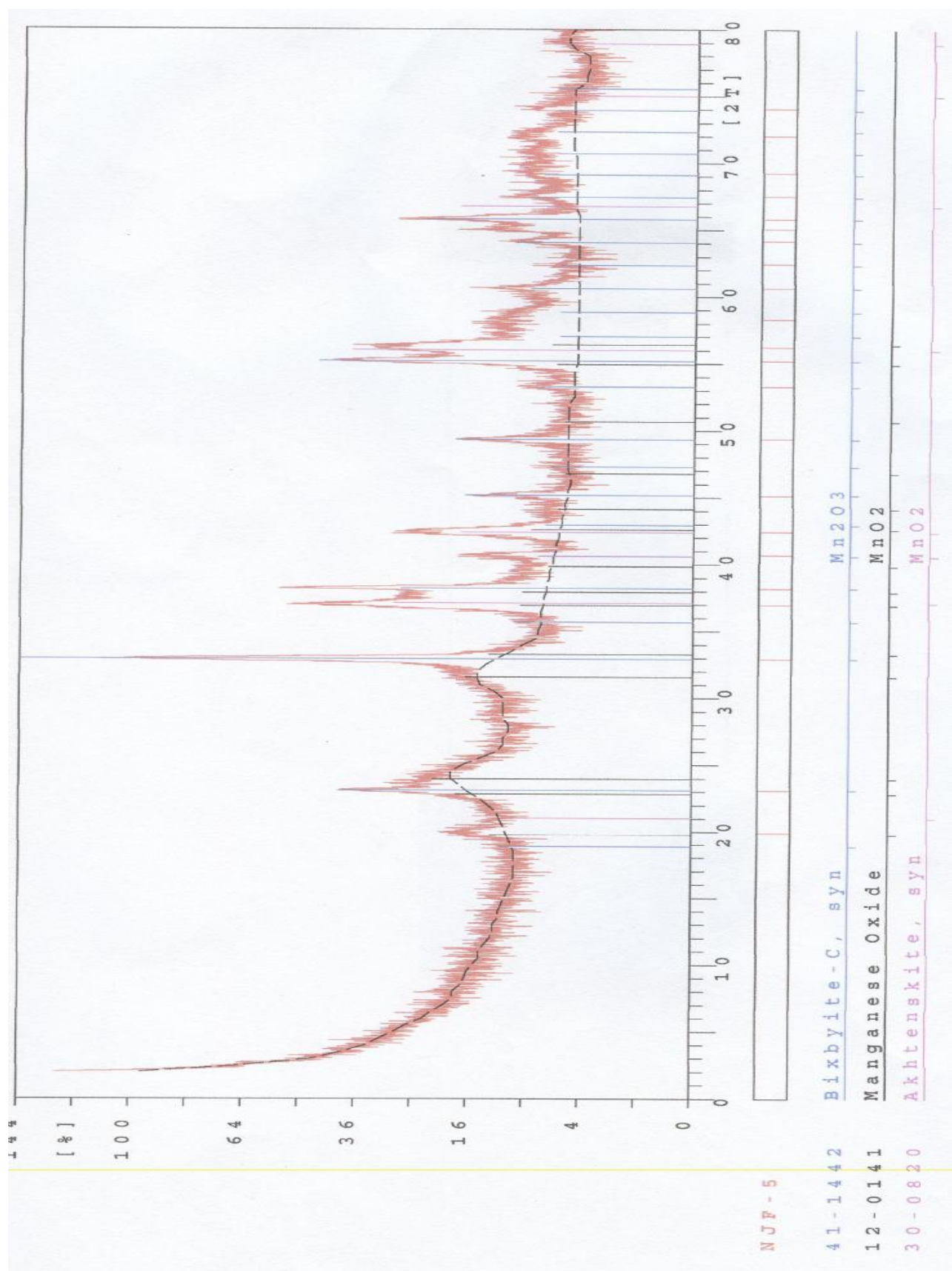
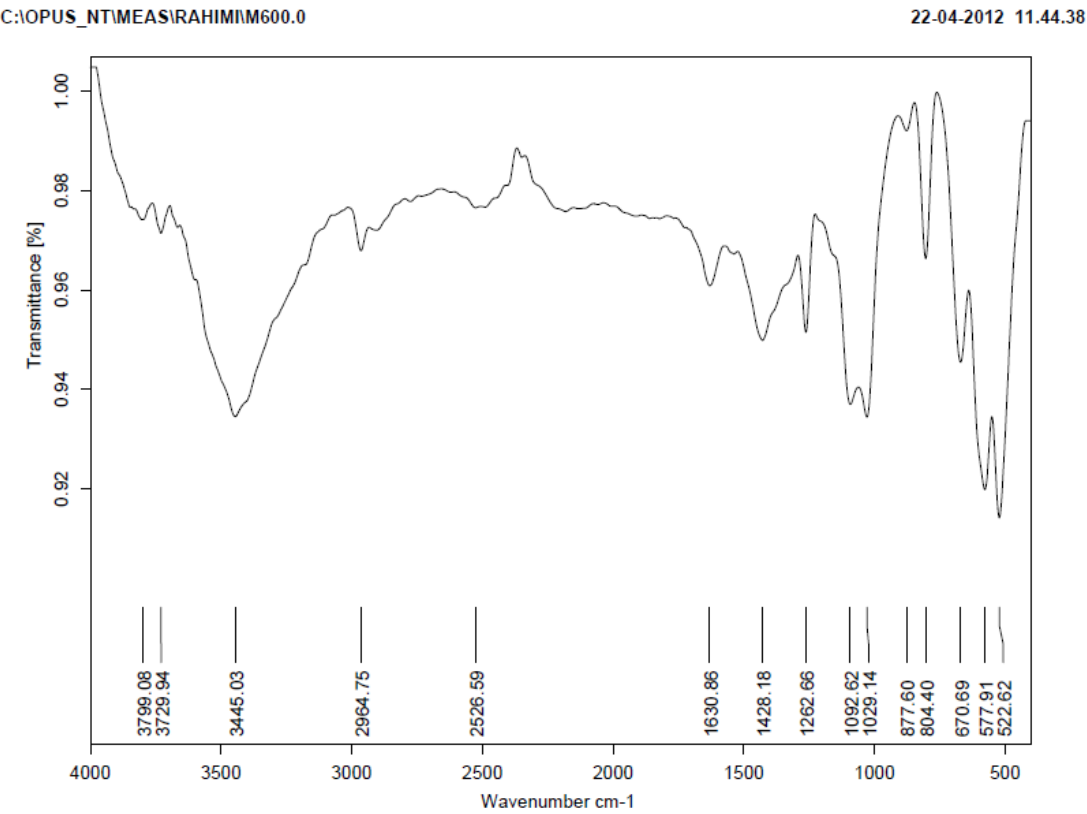
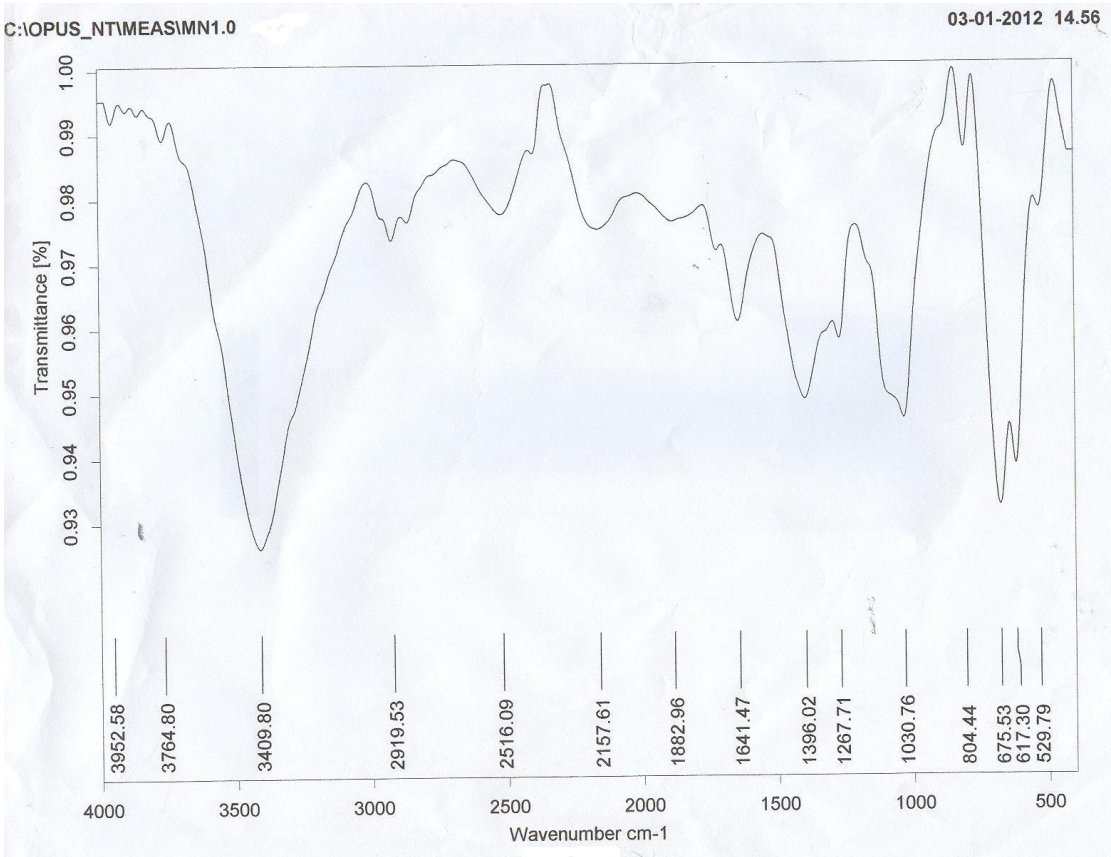
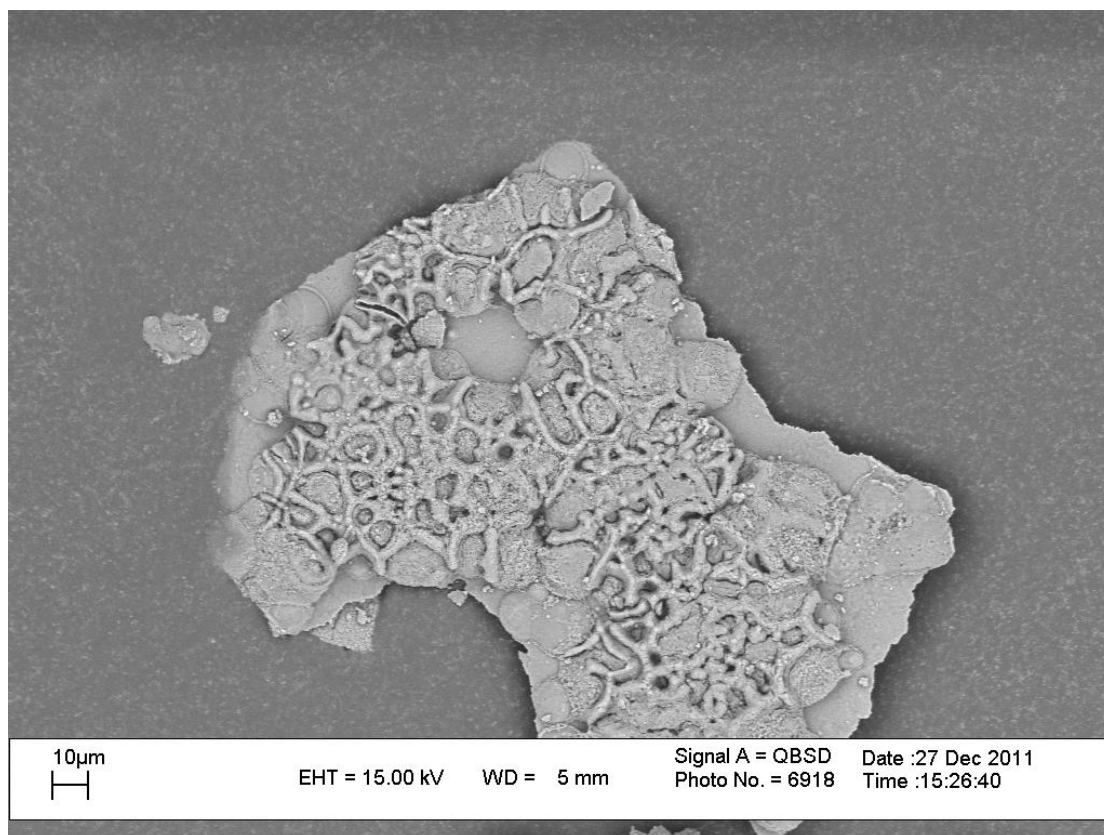


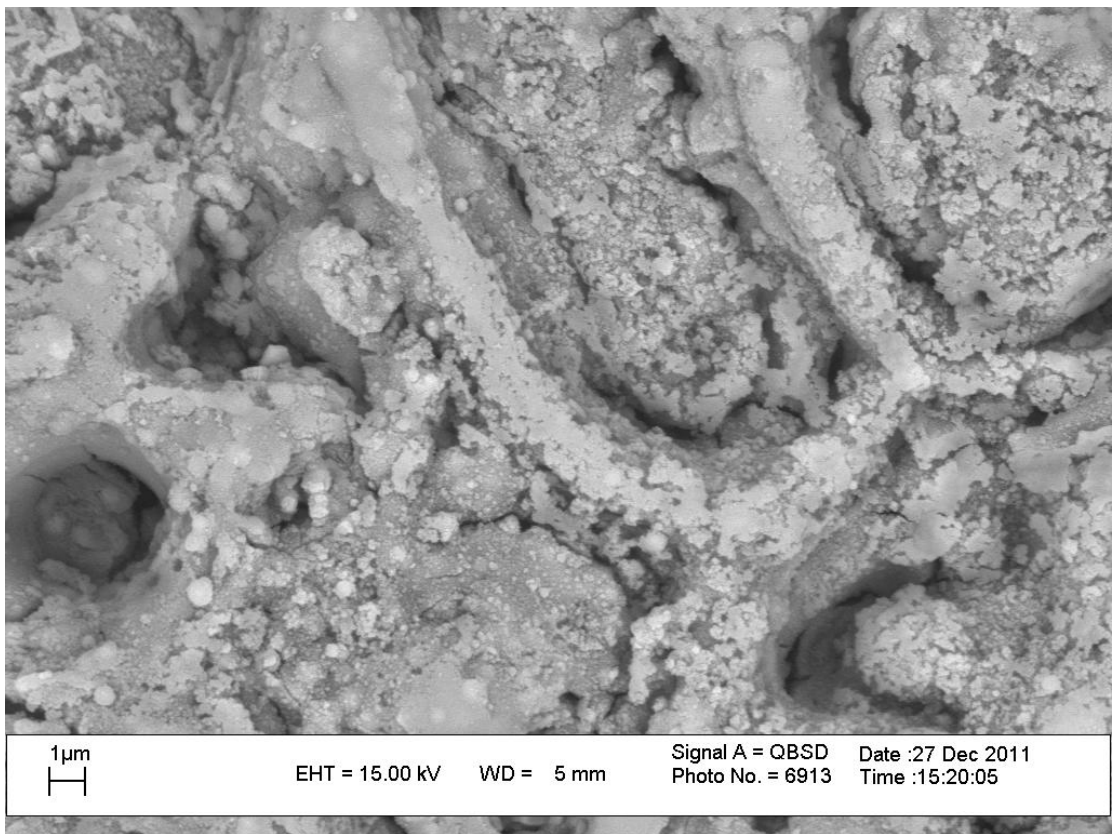
Fig. S2 XRD patterns of the obtained the nano-sized manganese oxide.



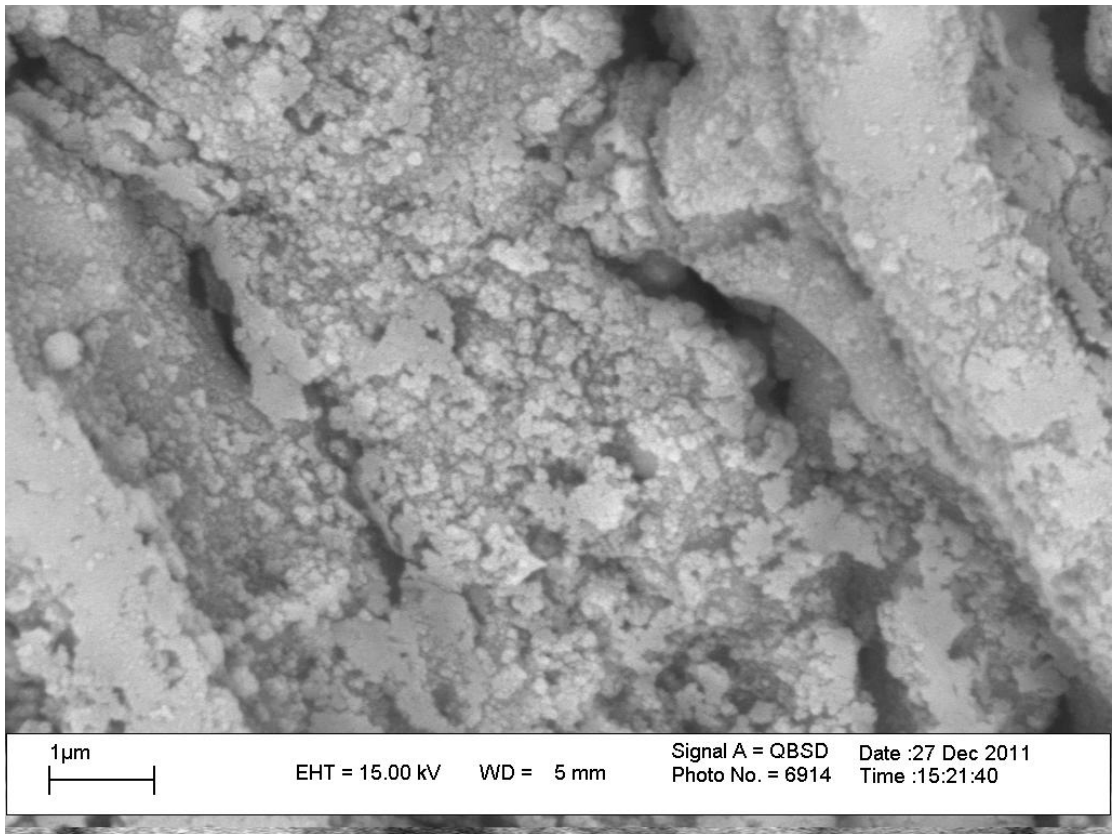
(b)
Fig. S3 IR spectra of sample calcined at 100 (top), and 600 °C (bottom)



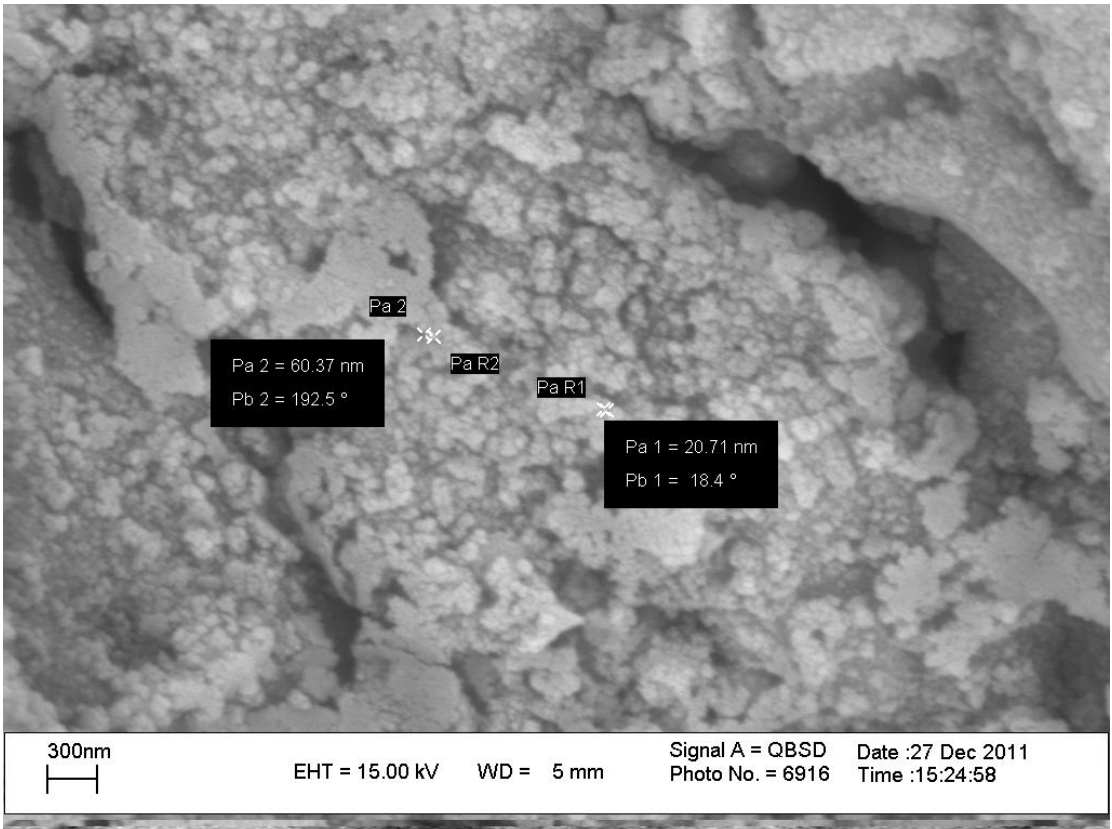
(a)



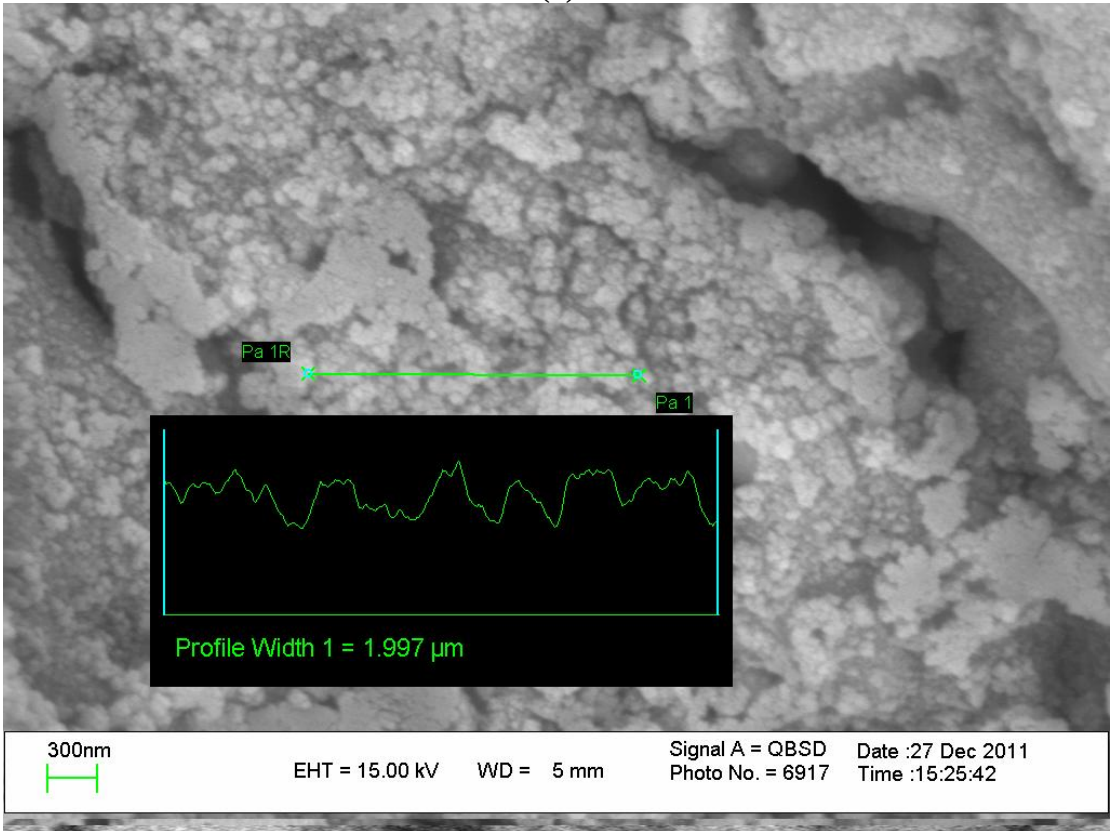
(b)



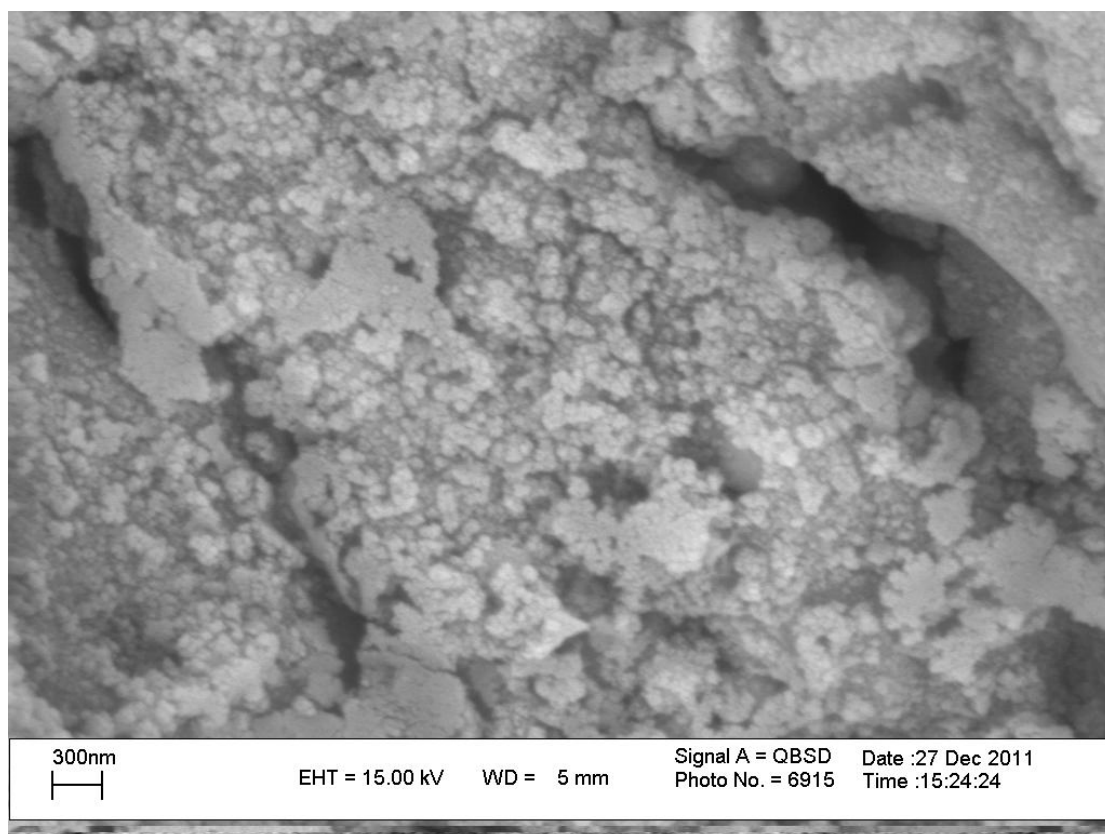
(c)



(d)



(e)

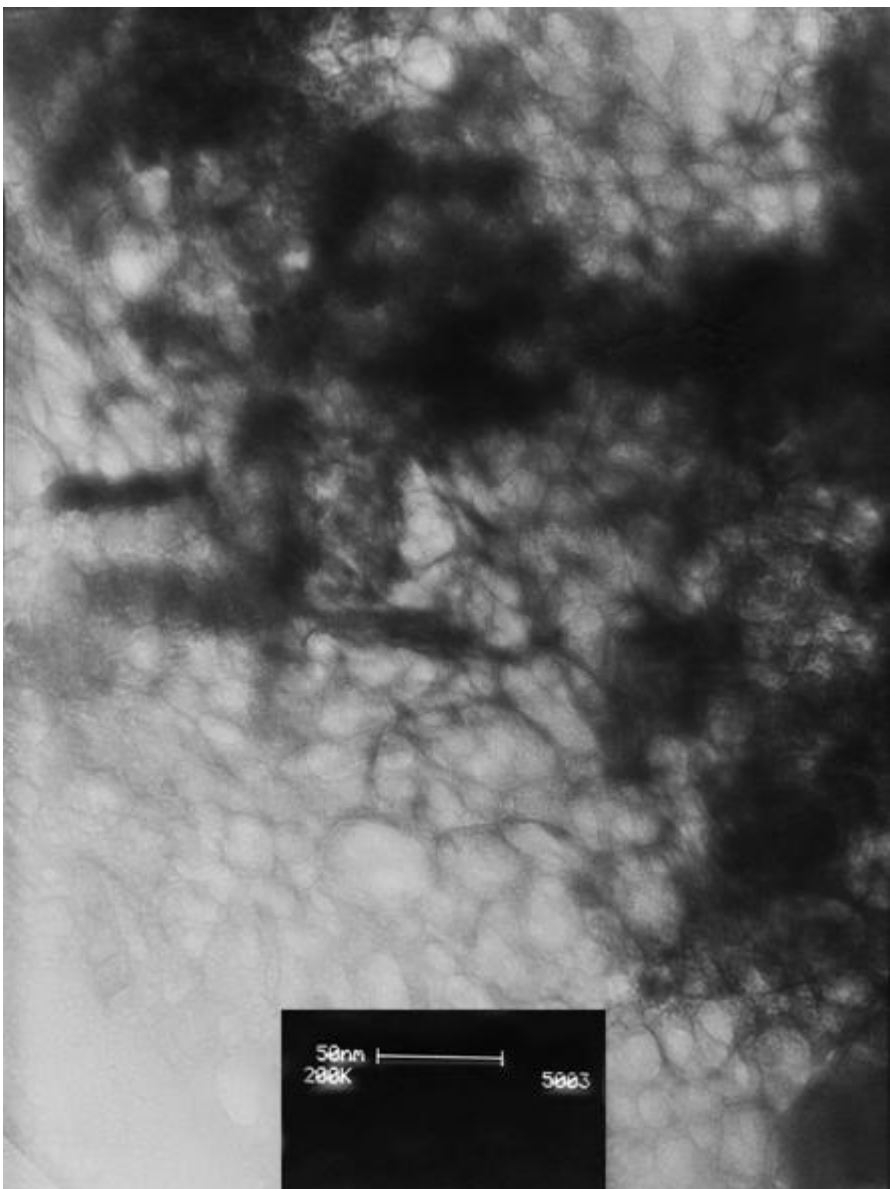


(f)

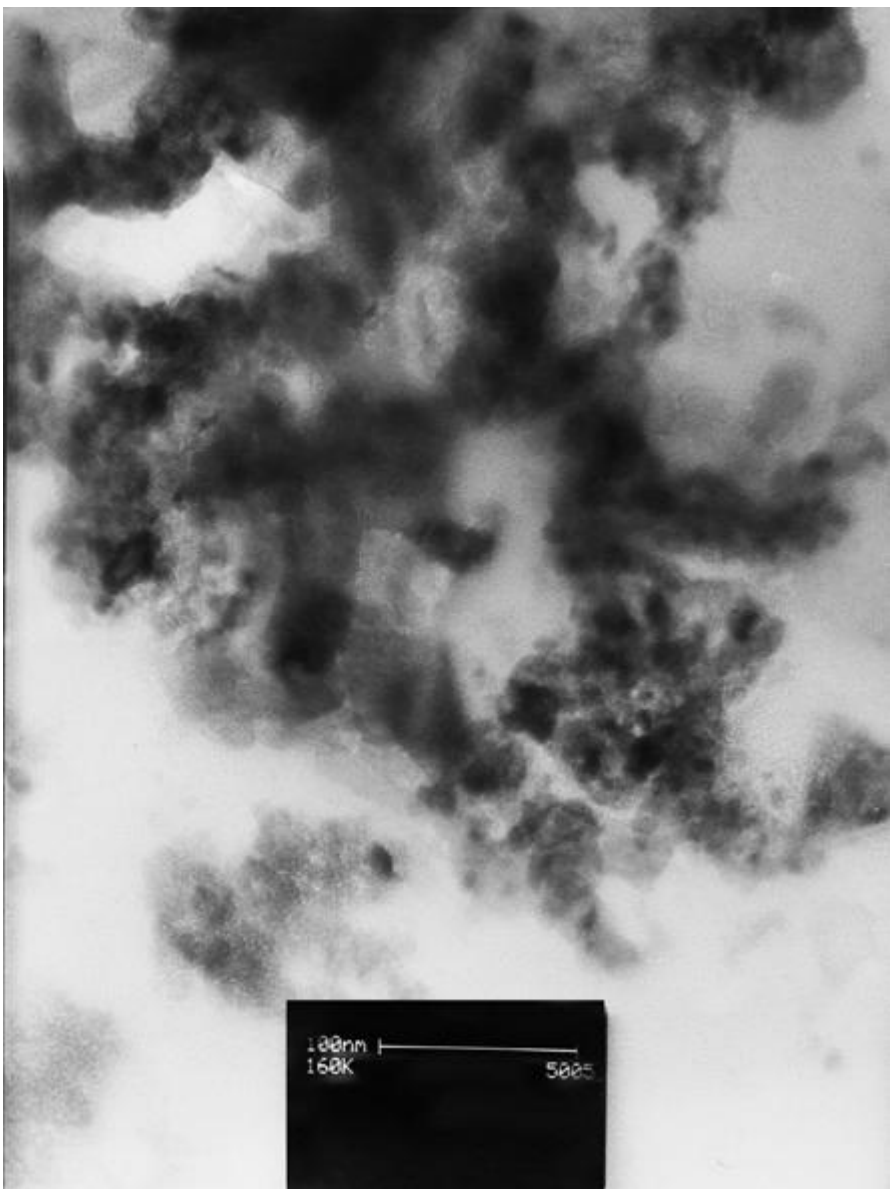
Fig. S4 SEM images of nano-sized manganese oxide (a-f).



(a)



(b)



(c)



(d)

Fig. S5 TEM images of zinc - manganese oxides prepared at 300 °C (a-d).

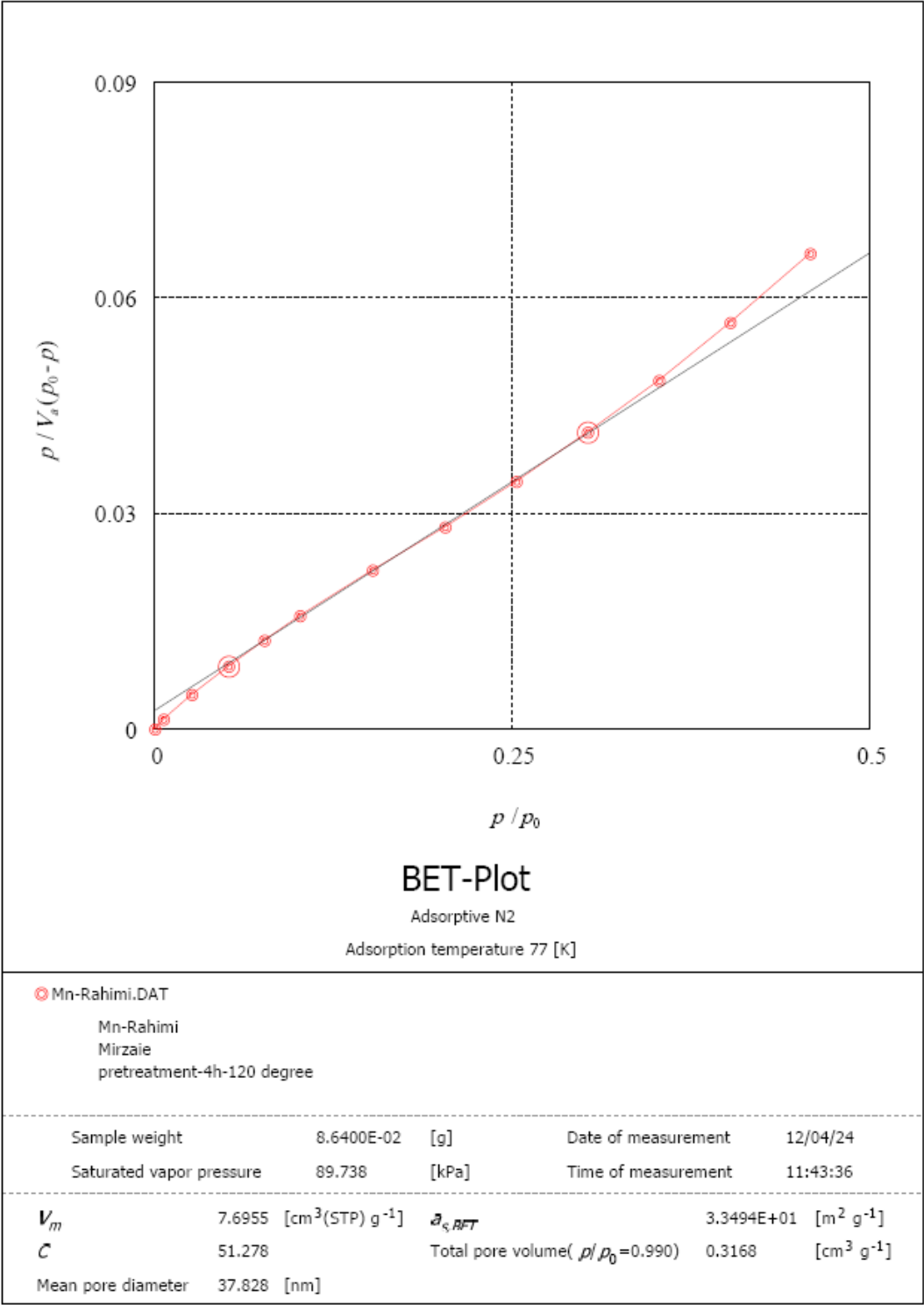


Fig. S6 The BET plot for prepared sample.

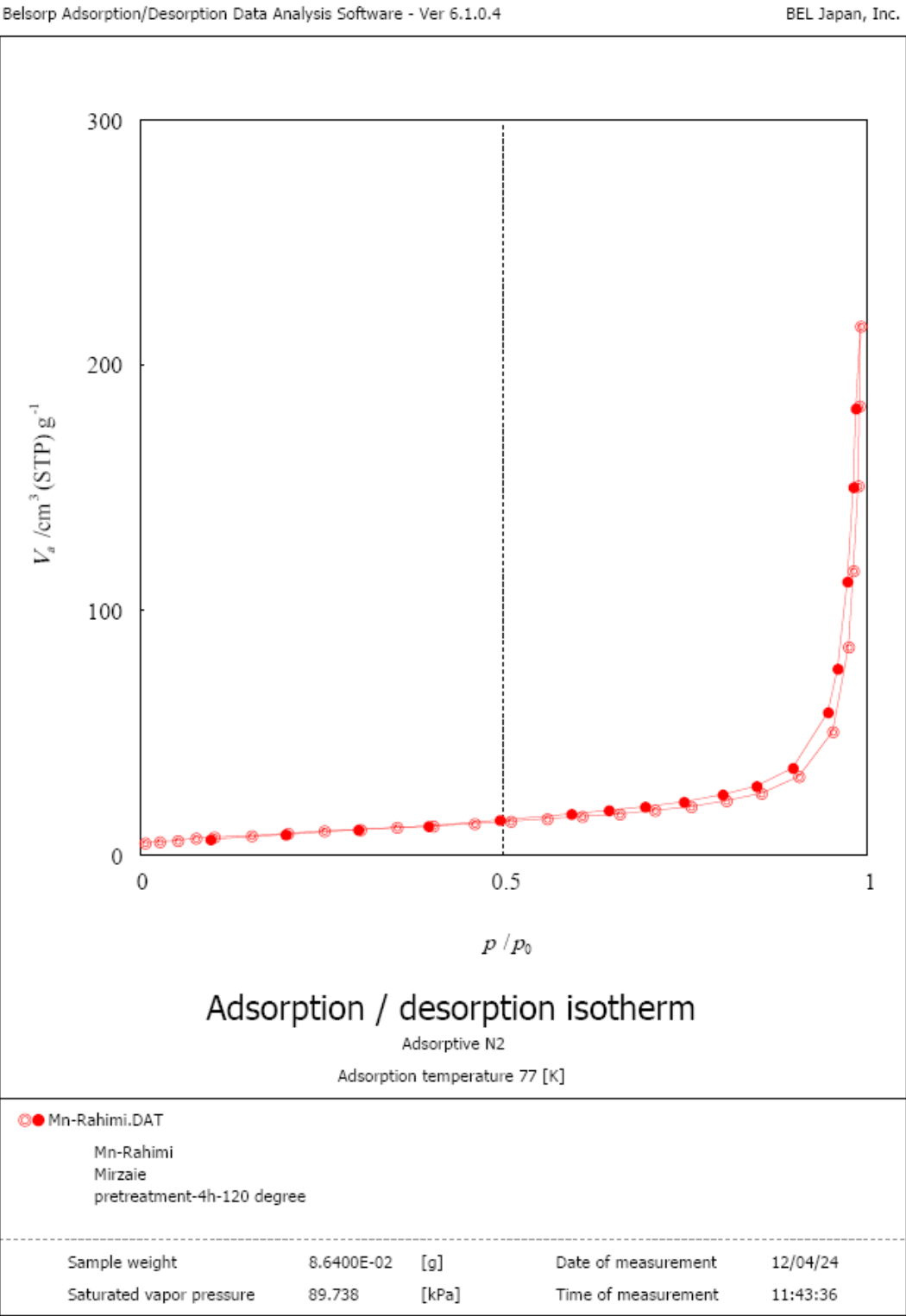
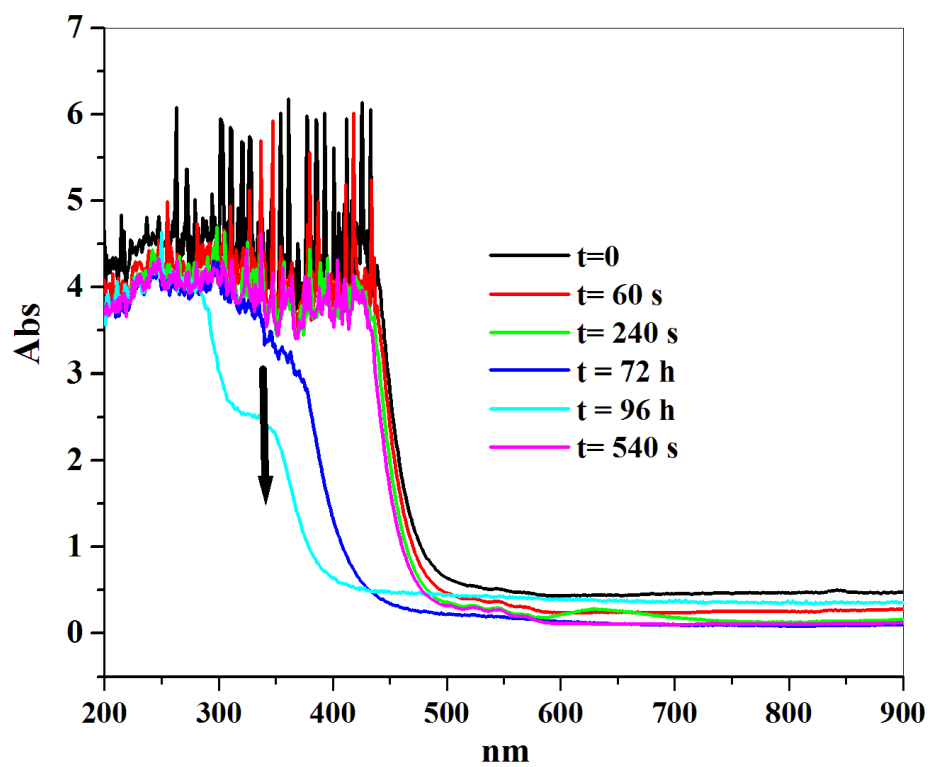
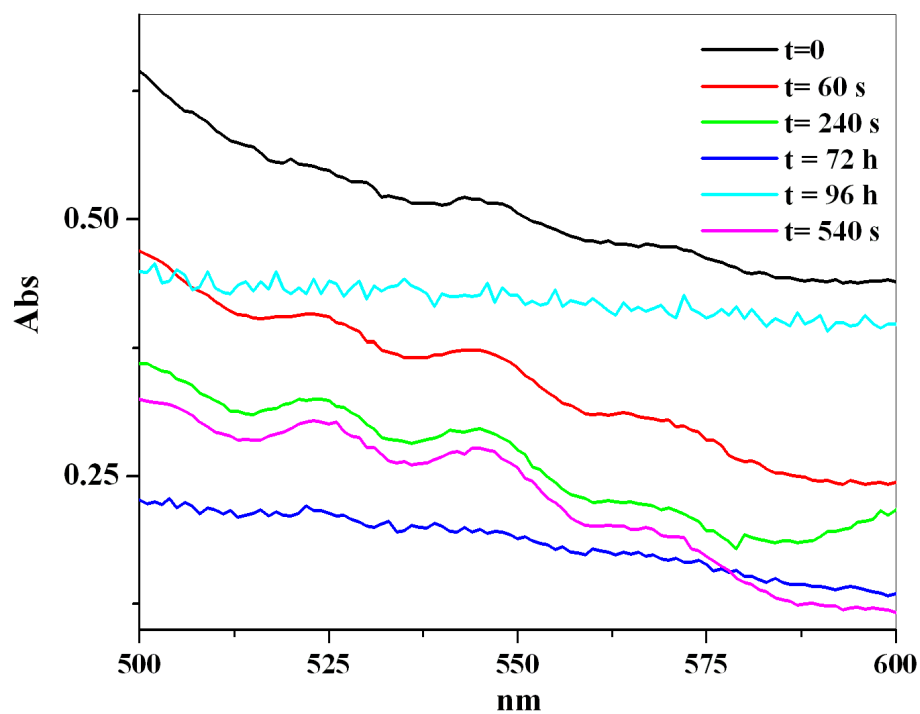


Fig. S7 The Adsorption / desorption isotherm plot for prepared sample.



(a)



(b)

Fig. S8 UV-vis spectra of the catalyst (10.0 mg) in Ce(IV) (0.4 M). The reduction of Ce(IV) (top) and MnO_4^- formation (bottom) could be observed in the first hours.

Table S1 The rate of water oxidation by the various manganese oxides
as catalysts for water oxidation.

Compound	Oxidant	TOF ^a	References
Nano-sized manganese oxide	Ce(IV)	0.15	This work
Octahedral Molecular Sieves	Ru(bpy) ₃ ³⁺	0.11	1
	Ce(IV)	0.05	
Octahedral Layered	Ru(bpy) ₃ ³⁺	0.028	1
	Ce(IV)	0.0047	
Amorphous Manganese Oxides	Ru(bpy) ₃ ³⁺	0.06	1
	Ce(IV)	0.52	
CaMnO ₃	Ce(IV)	0.012	2
Ca ₂ Mn ₃ O ₈	Ce(IV)	0.016	2
CaMn ₂ O ₄ ·H ₂ O (Nano particles)	Ce(IV)	2.2	3
CaMn ₃ O ₆	Ce(IV)	0.046	4
CaMn ₄ O ₈	Ce(IV)	0.035	4
CaMn ₂ O ₄ ·4H ₂ O	Ce(IV)	0.32	5
CaMn ₂ O ₄ ·H ₂ O	Ce(IV)	0.54	5
Mn ₂ O ₃	Ce(IV)	0.027	5
α-MnO ₂ nanotubes	Ru(bpy) ₃ ³⁺	0.035	6
α-MnO ₂ nanowires	Ru(bpy) ₃ ³⁺	0.059	6
β-MnO ₂ nanowires	Ru(bpy) ₃ ³⁺	0.02	6
Bulk α-MnO ₂	Ru(bpy) ₃ ³⁺	0.01	6
Mn oxide nanoclusters	Ru(bpy) ₃ ³⁺	0.28	7
MnO ₂ (colloid)	Ce(IV)	0.09	8
PSII	Sunlight	25000	9

^a mmol O₂/mol Mn per second. In these calculations, it is assumed that all deposited metal centers are involved in the catalysis, so lower TOF limits are calculated.

References:

- 1 A. Iyer, J. Del-Pilar, C. Kithongo King'ondur, E. Kissel, H. Fabian Garces, H. Huang, A. M. El-Sawy, P. K. Dutta and S. L. Suib, *J. Phys. Chem. C*, DOI: 10.1021/jp2120737.
- 2 M. M. Najafpour, S. Nayeri and B. Pashaei, *Dalton Trans.*, doi: 10.1039/C2DT12189A
- 3 M. M. Najafpour, S. Nayeri and B. Pashaei, *Dalton Trans.*, **40**, 2011, 9374.
- 4 M. M. Najafpour, *Dalton Trans.*, 2011, **40**, 3793.
- 5 M. M. Najafpour, T. Ehrenberg, M. Wiechen and P. Kurz, *Angew. Chem., Int. Ed.*, 2010, **49**, 2233.
- 6 V. B. R. Boppana and F. Jiao, *Chem. Commun.*, 2011, **47**, 8973.
- 7 Y. Okuno, O. Yonemitsu and Y. Chiba, *Chem. Lett.*, 1983, 815.
- 8 M. M. Najafpour, *Dalton Trans.*, 2011, **40**, 3805.
- 9 C. Tommos and G. T. Babcock, *Biochim. Biophys. Acta, Gen. Subj.*, 2000, **1458**, 199.