

Visible light assisted synthesis of manganese oxide nanoparticles at room temperature

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The Raman spectra realized on the synthesized λ -MnO₂ was compared to the bulk λ -MnO₂. It can be observed that the same peaks are detected which confirms that the synthesized oxide is indeed λ -MnO₂. In addition, it can be noticed that the main peak of the synthesized material is broader and shifted to the higher frequencies due certainly to the nanometric size of the particles.

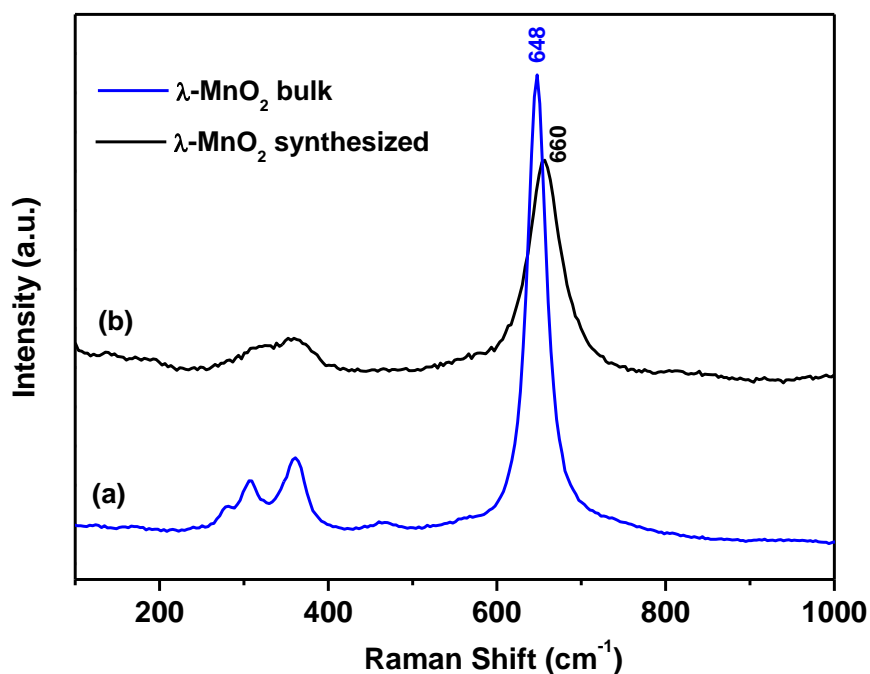


Fig. S1: Raman spectra of (a) λ -MnO₂ bulk and (b) λ -MnO₂ synthesized by VIS irradiation in the presence of NaOH

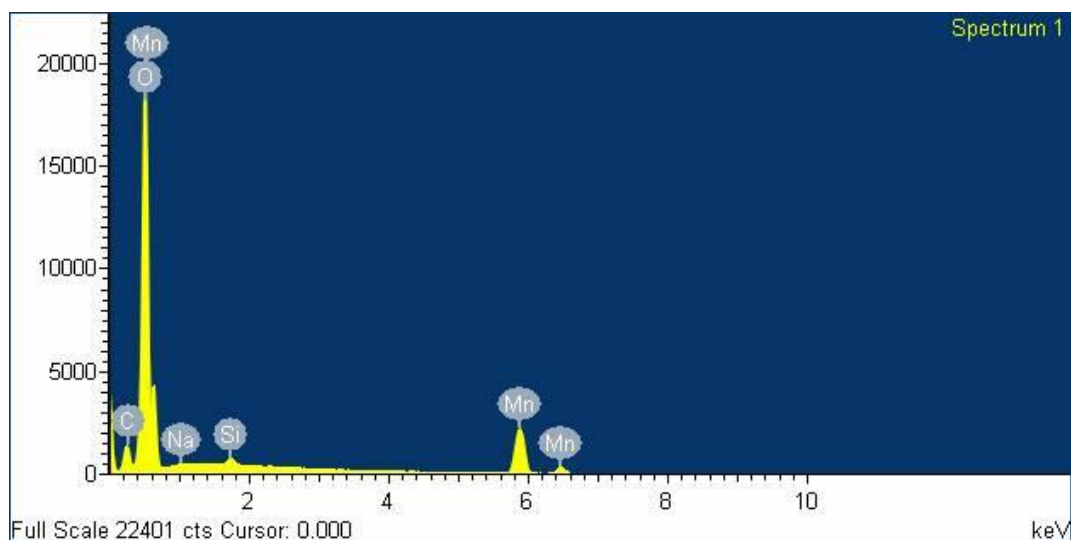


Fig. S2: EDX spectra of a manganese oxide obtained by irradiation in the presence of NaOH

Table S1: Composition of manganese oxide determined by EDX

Element	Mn	O	Na	*C	*Si
wt. %	63.4	31.6	0.15	4.2	0.53

*The C and Si are coming from the substrate used to perform the EDX analysis

Figure S3a and b shows the morphology of manganese oxide obtained using manganese nitrate and manganese chloride in air. In the first case, a mixture of nanoparticles (γ - Mn_3O_4) and nanotubes (λ - MnO_2) is obtained while the second case only nanoparticles of γ - Mn_3O_4 are formed. It is clear that a counter anion which not contains oxygen, hence a reaction medium poorer in oxygen, favors the formation of oxides with lower oxidation state. This supports also the results obtained with manganese nitrate but in a nitrogen richer medium when the same morphology and crystalline phase was obtained (Fig. S3c).

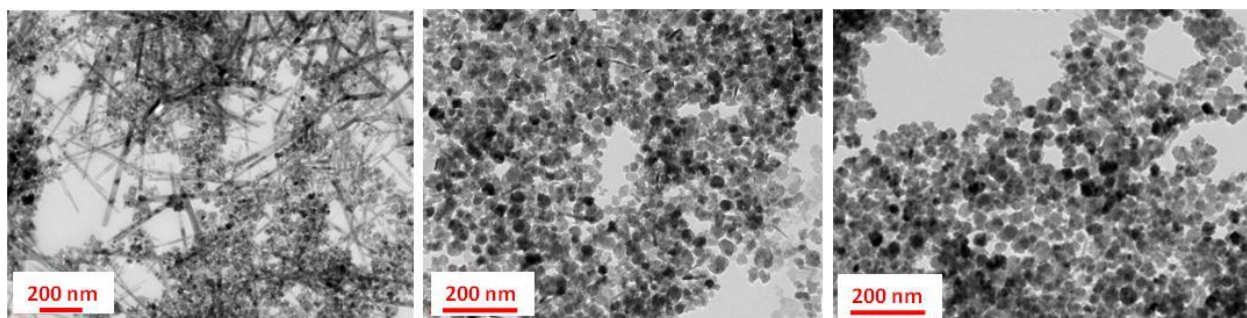


Fig. S3: TEM pictures of manganese oxides prepared by using (a) manganese nitrate-air (b)manganese chloride-air and (c)manganese nitrate-1h-rich N_2 air atmospheres. (irradiation time 1h, in the LiOH presence)

Figure S4 shows the UV-Vis absorption spectra of $Mn(NO_3)_2$ 0.1M in aqueous solution, that exhibits an absorption band located in the 260-340 nm range (Fig. S4a). Upon addition of hydroxide (NaOH 4.8 mM) in the precursor solution, a new absorption appears on the whole visible range. It corresponds to Rayleigh scattering by submicrometric particles with the characteristic $1/\lambda^4$ wavelength dependence range (Fig S4b). It is due to new species (clusters) formed upon addition of hydroxide. After a 1h irradiation of this suspension, an autophotocatalytic process takes place, thus inducing an important increase of the amount of particles that goes in line with a huge increase of the apparent absorption due to light scattering (Fig S4c).

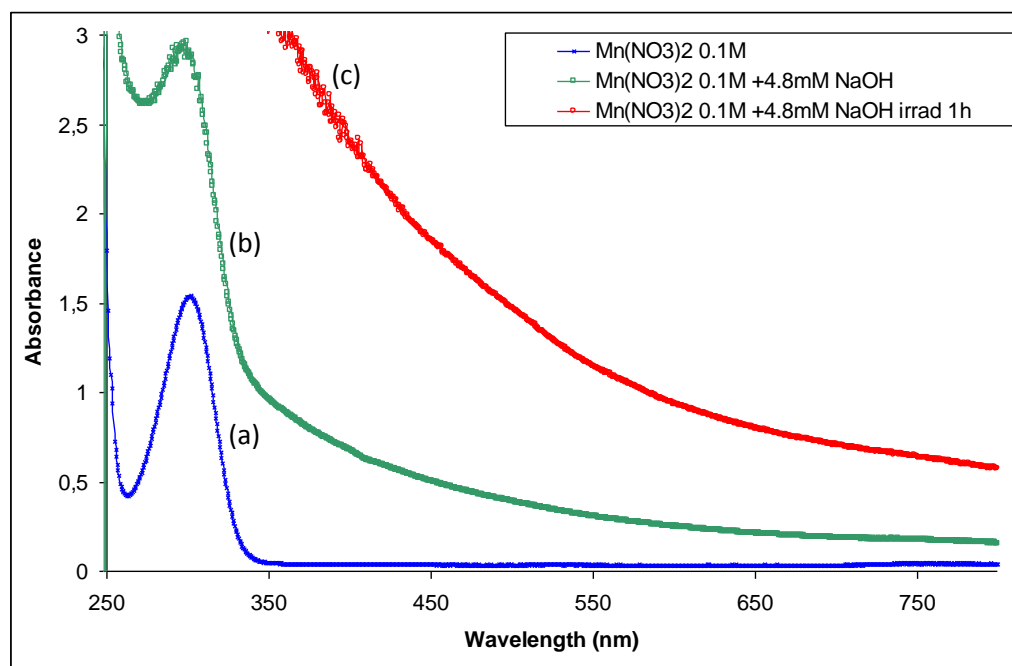


Fig. S4: UV-Visible absorption spectra of $Mn(NO_3)_2$ solution (a) $Mn(NO_3)_2$ with 4.8mM NaOH (b) and $Mn(NO_3)_2$ with 4.8mM NaOH after 1h irradiation.

The influence of the irradiation time (1h, 3h and respectively 24h) on the manganese oxide morphology and structure was evaluated for the LiOH systems. The TEM pictures (Fig. S5) show no significant morphology difference when varying this parameter but structural modifications are clearly see by XRD and Raman spectroscopy (Fig. S6).

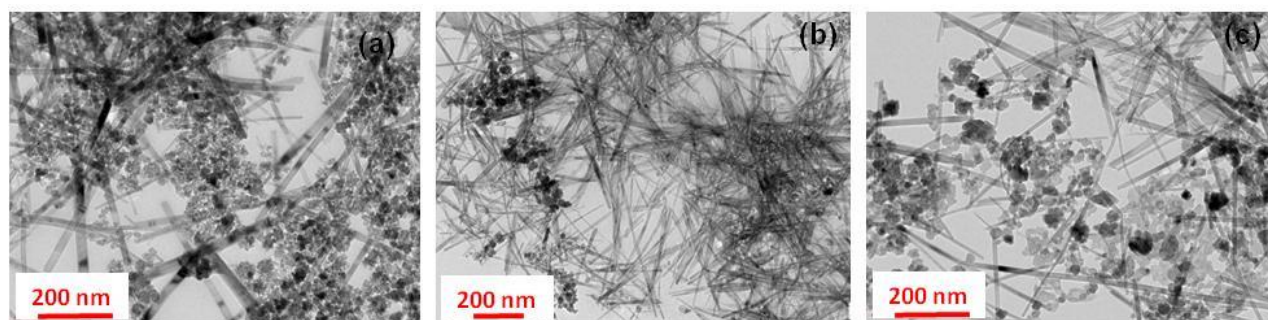


Fig.S5: TEM pictures of manganese oxides prepared using of LiOH and different irradiation time exposure: (a) 1h (b) 3h and (c) 24h;

The Raman spectra of the manganese oxides synthesized at 1h, 3h and 24h irradiation times are presented in Fig. S6. After 1h of irradiation the obtained manganese oxide is a mixture of γ - Mn_3O_4 and λ - MnO_2 phases. When the irradiation time increases to 3h the most intense peak (660 cm^{-1}) significantly decrease and after 24 h irradiations specific peaks corresponding to a mixture γ - Mn_3O_4 , λ - MnO_2 and $MnOOH$ are seen.

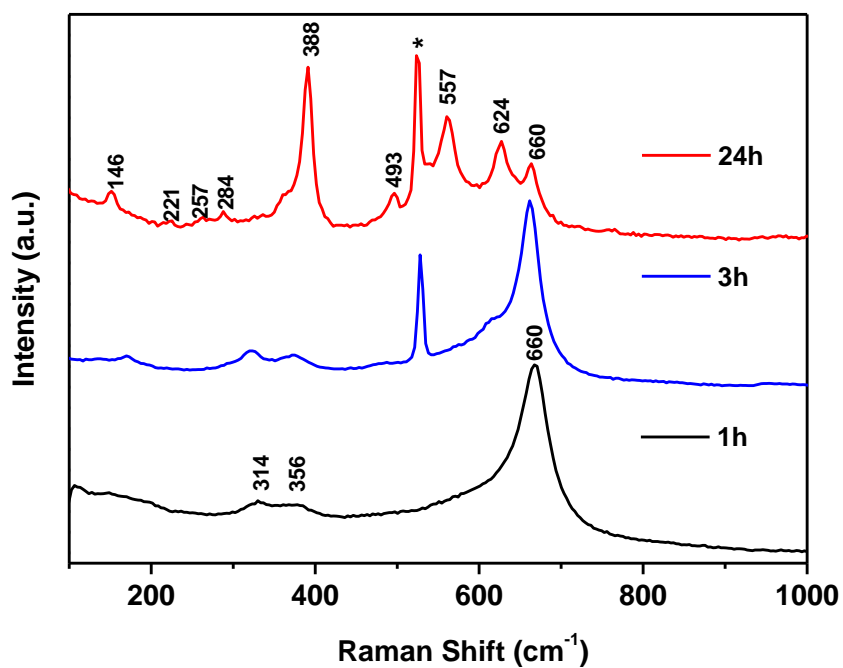


Fig.S6: Raman spectra of manganese oxides prepared using of LiOH and different irradiation time exposure: (a) 1h (b) 3h and (c) 24h;

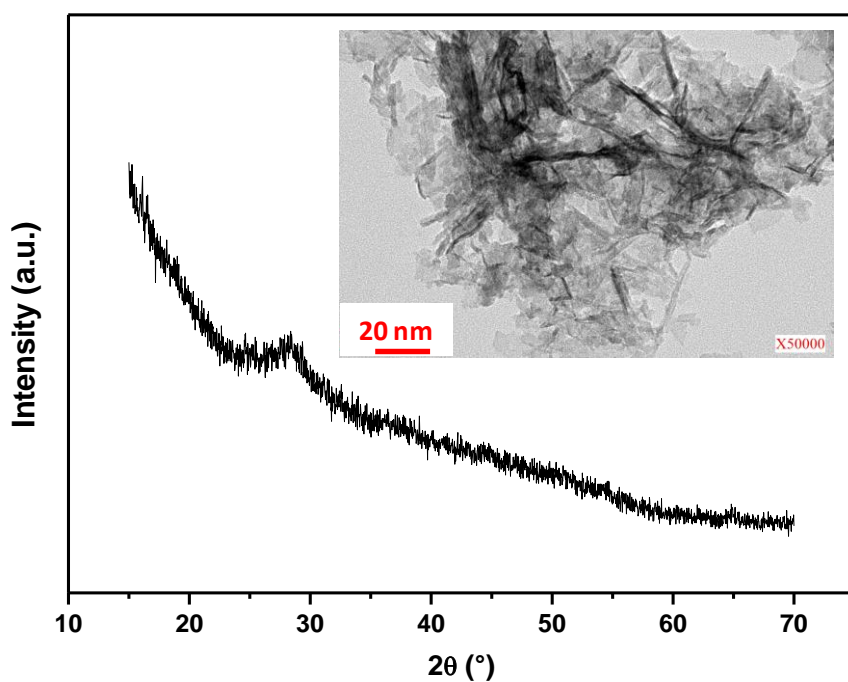


Fig. S7: XRD patterns and TEM image of a material obtained in the presence of LiOH under pure N_2 atmosphere (1h irradiation)

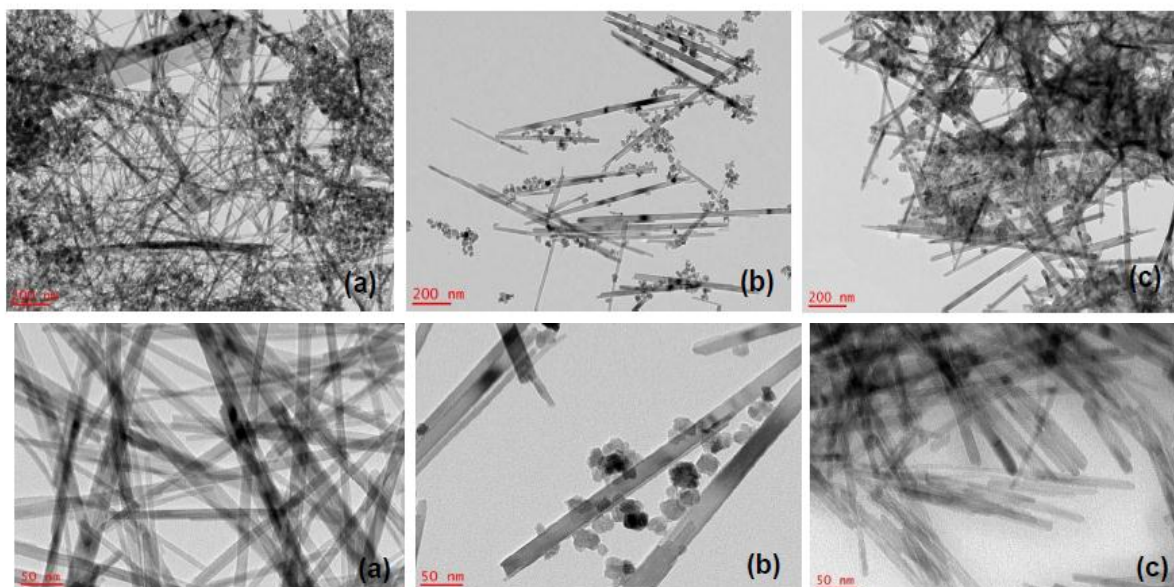


Fig. S8: TEM pictures of manganese oxides prepared with different precursor solution concentration: (a) 0.1 M (b) 0.4 M and (c) 0.8 M in the presence of LiOH;

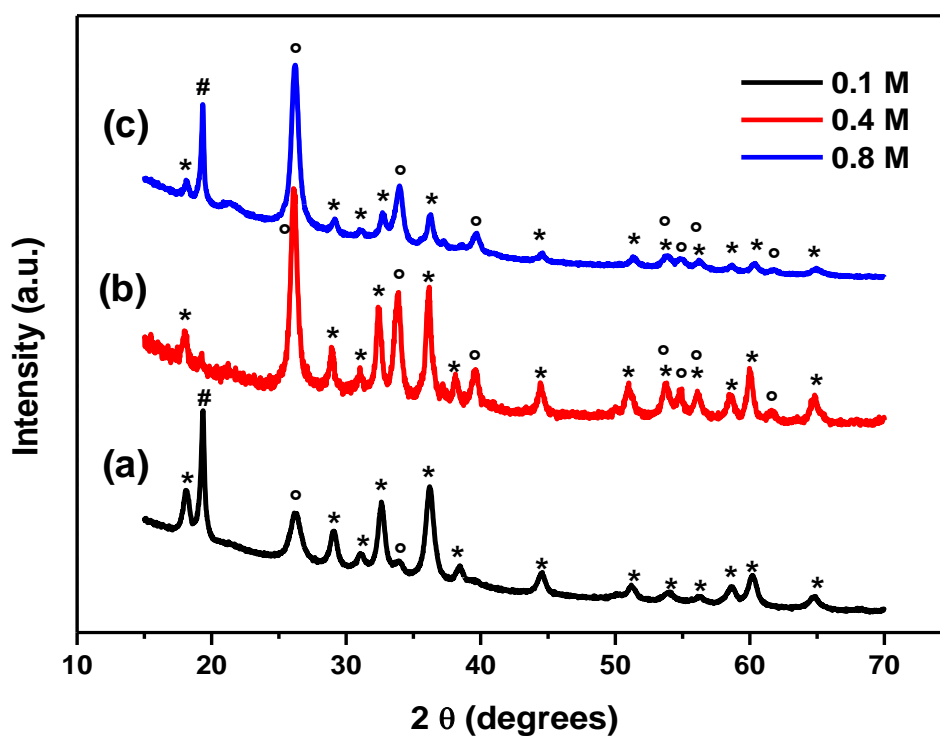


Fig. S9: XRD patterns of manganese oxides prepared with different precursor solution concentration: (a) 0.1 M (b) 0.4 M and (c) 0.8 M in the presence of LiOH;

Table S2: Synthesis parameters used along with the formed products and their characteristics

No.	Precursor	Hydroxide	[Mn ²⁺] (mol/L)	[HO ⁻] (mmol/L)	Time (hours)	Atmosphere	Phase	Morphology	Size (nm)
1	Mn(NO ₃) ₂ •4H ₂ O	NaOH	0.1	4.8	24	air	γ-Mn ₃ O ₄	Spheres	6-8
2	Mn(NO ₃) ₂ •4H ₂ O	NaOH	0.4	4.8	24	air	λ-MnO ₂	Rods	L:50-150 D: 2-5
3	Mn(NO ₃) ₂ •4H ₂ O	NaOH	0.8	4.8	24	air	λ-MnO ₂	Rods	L:50-100 D:5-7
4	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.1	4.8	24	air	λ-MnO ₂ + γ-Mn ₃ O ₄ + MnO(OH)	Flowers Rods	30 L:1500-2500 D: 10
5	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	4.8	24	air	λ-MnO ₂ + γ-Mn ₃ O ₄ + MnO(OH)	Flowers Rods	30-40 L:1000-1200 D: 10-15
6	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.8	4.8	24	air	λ-MnO ₂ + γ-Mn ₃ O ₄ + MnO(OH)	Flowers Rods	30 L:800-1000 D: 7-10
7	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	2.4	24	air	λ-MnO ₂	Rods	L: 200-300 D:2-5
8	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	7.8	24	air	λ-MnO ₂ + γ-Mn ₃ O ₄ + MnO(OH)	Cubes Rods	30 L:1000-1500 D:15-25
9	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	4.8	1	air	λ-MnO ₂ + γ-Mn ₃ O ₄	Rods Flowers	L:300-500 D:20 D:40
10	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	4.8	3	air	λ-MnO ₂ + γ-Mn ₃ O ₄ + MnO(OH)	Flowers Rods	30-40 L:1000-1200 D: 10-15
11	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	4.8	1	O ₂	λ-MnO ₂	Rods	L:50-100 D:5-7
12	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	4.8	1	Air-N ₂	γ-Mn ₃ O ₄	Flowers	40
13	Mn(NO ₃) ₂ •4H ₂ O	LiOH	0.4	4.8	1	N ₂	-	-	-
14	Mn(NO ₃) ₂ •4H ₂ O	KOH	0.4	4.8	24	air	λ-MnO ₂	Rods	50-150
15	MnCl ₂	LiOH	0.4	4.8	1	air	γ-Mn ₃ O ₄	Cubes	20-25

