Electronic Supplementary Information

Electronic Supplementary Material (ESI) for RSC Advances

Mechanism of water oxidation by nanolayered manganese oxide: a step forward

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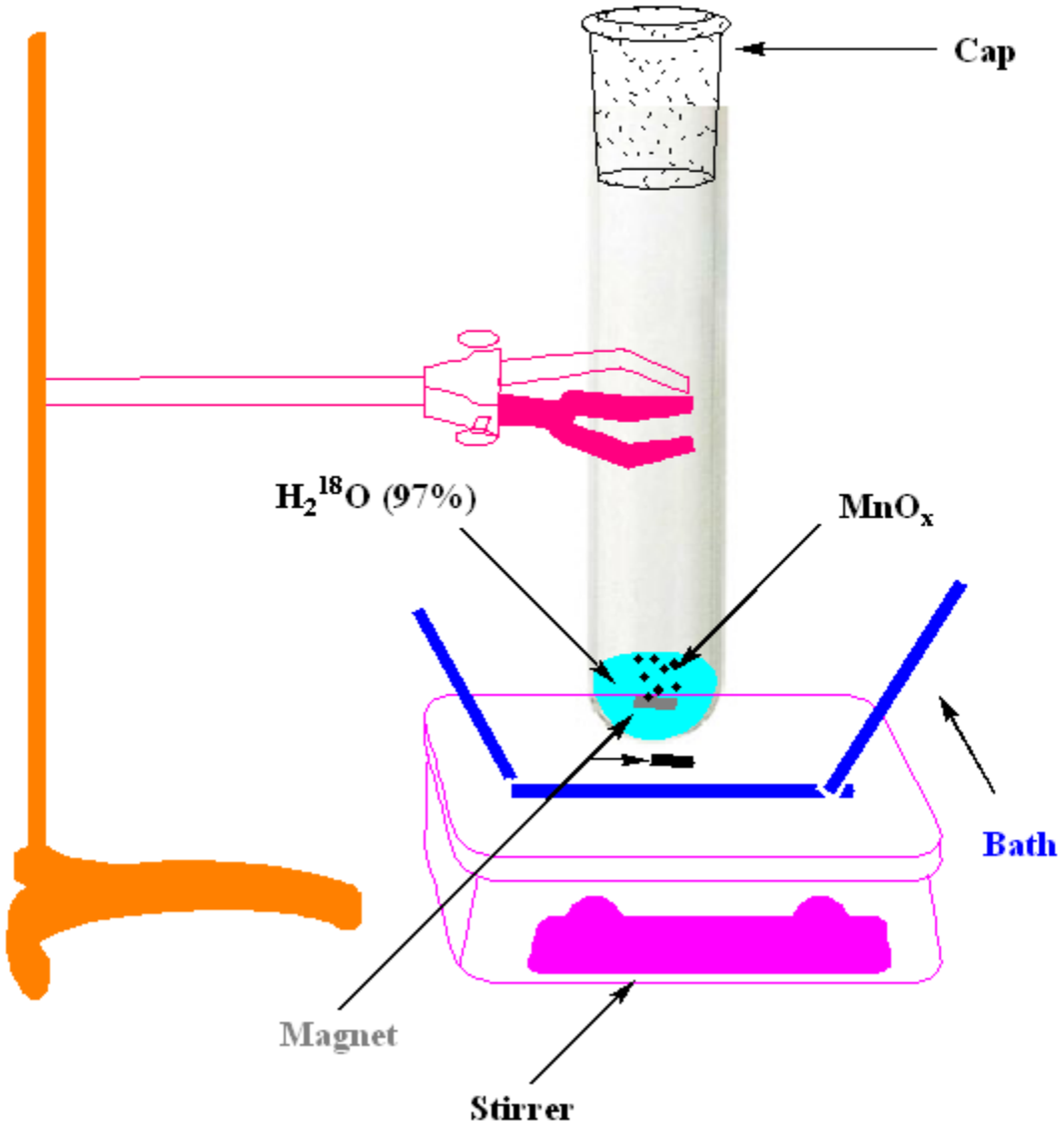
Material and methods

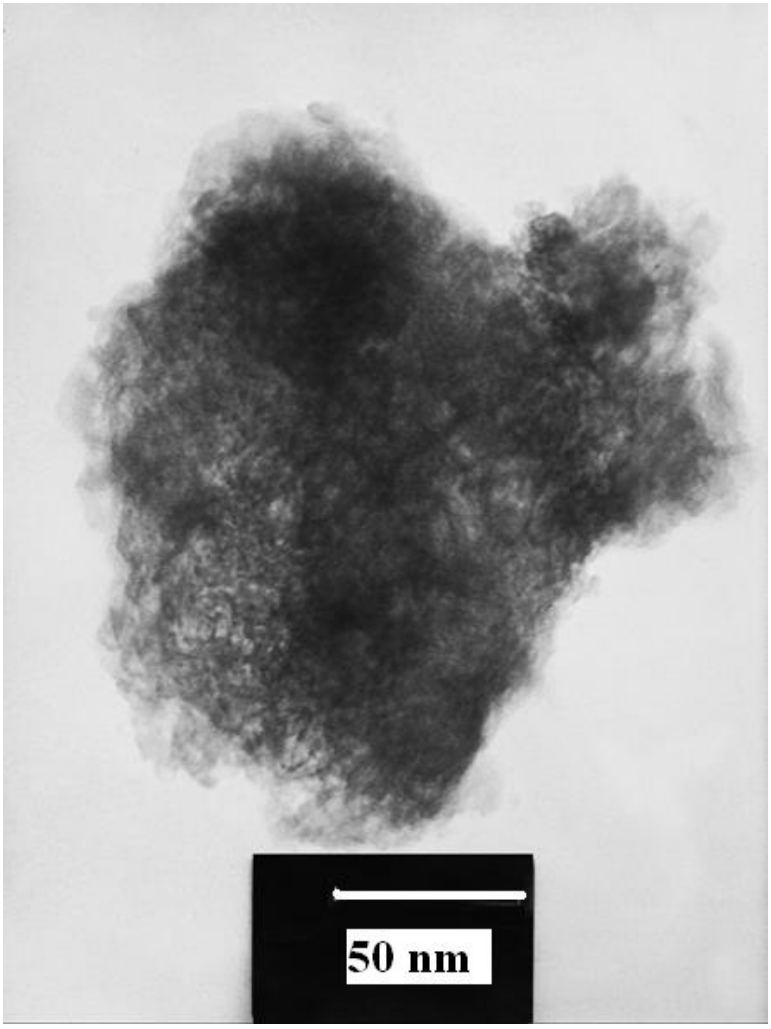
All reagents and solvents were purchased from commercial sources and were used without further purification. $H_2{}^{18}O$ (97%) was purchased from Aldrich. The oxide was synthesized by previously reported method (ref. S1).

Procedure

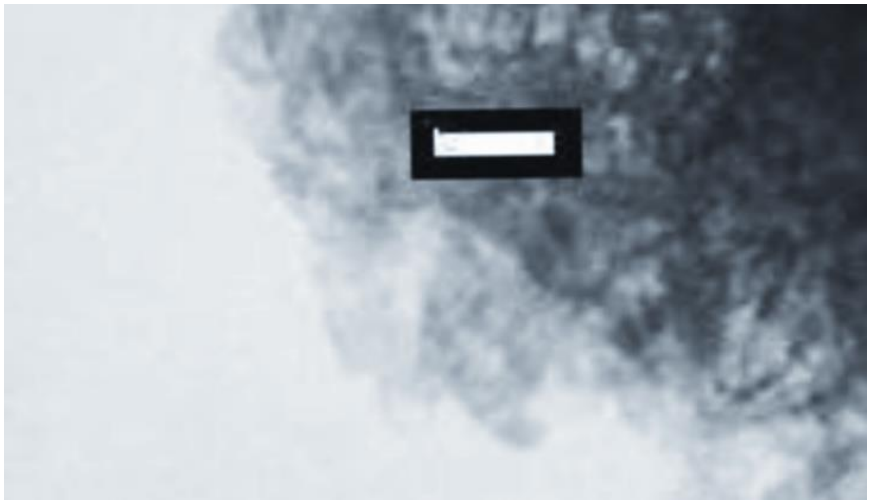
0.25 mL $H_2{}^{18}O$ (97%) was added to 125 mg K-Mn oxide in a small test tube. After different times, a few amounts of oxide were separated, added to Et_2O to remove water and stop water exchange, and dried under vacuum at room temperature (Scheme S1). As the reference compound, we used similar procedure by K-Mn oxide and treated it by $H_2{}^{16}O$.



Scheme S1 Set up for finding the rate of exchange for μ-O on the surface of layered Mn oxide by diffuse reflectance infrared Fourier transform spectroscopy.



a



b

Fig. S1 TEM images of nanolayered Mn-K. Scale bar in b is 12 nm.

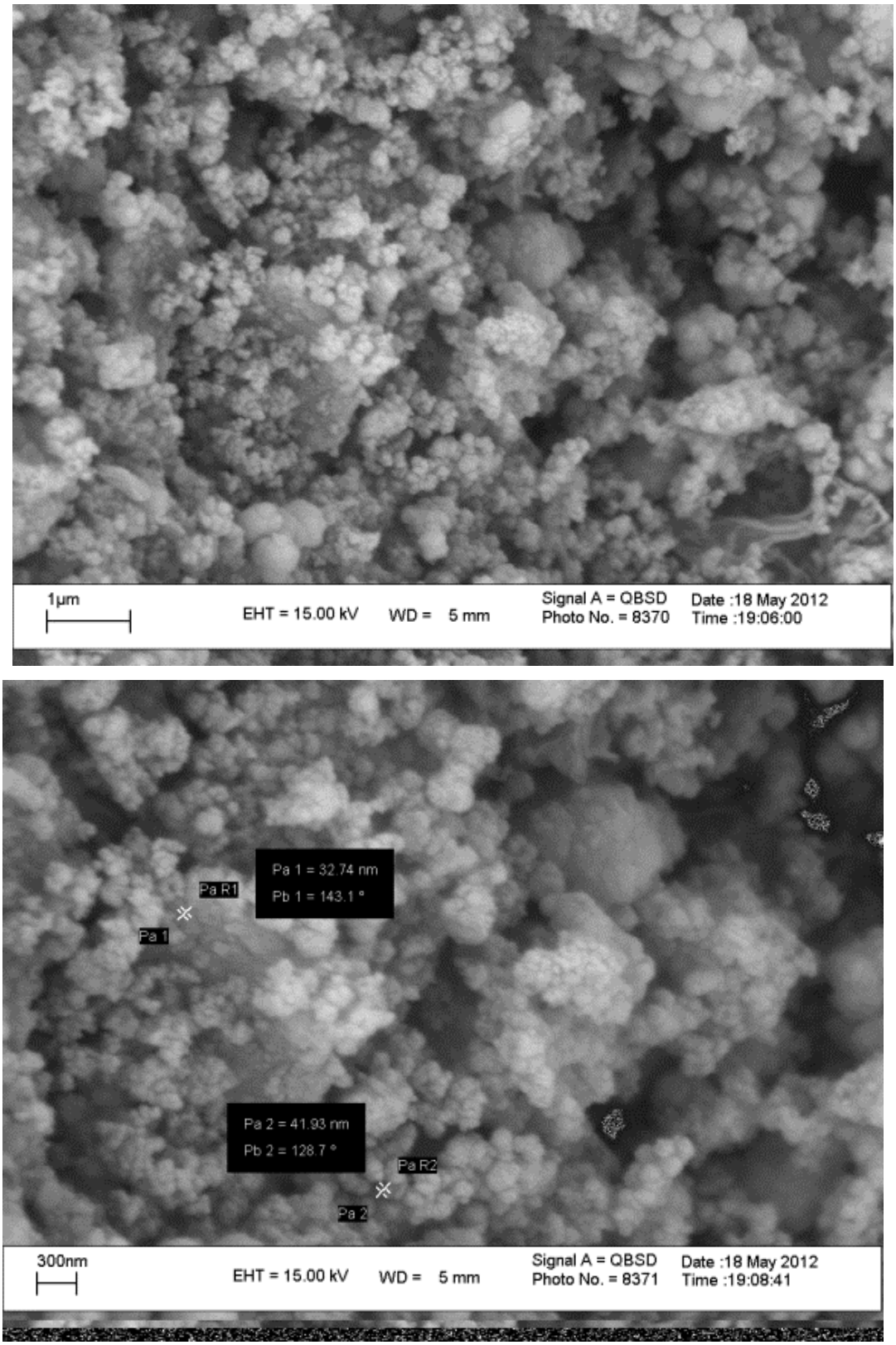


Fig. S2 SEM images of nanolayered Mn-K.

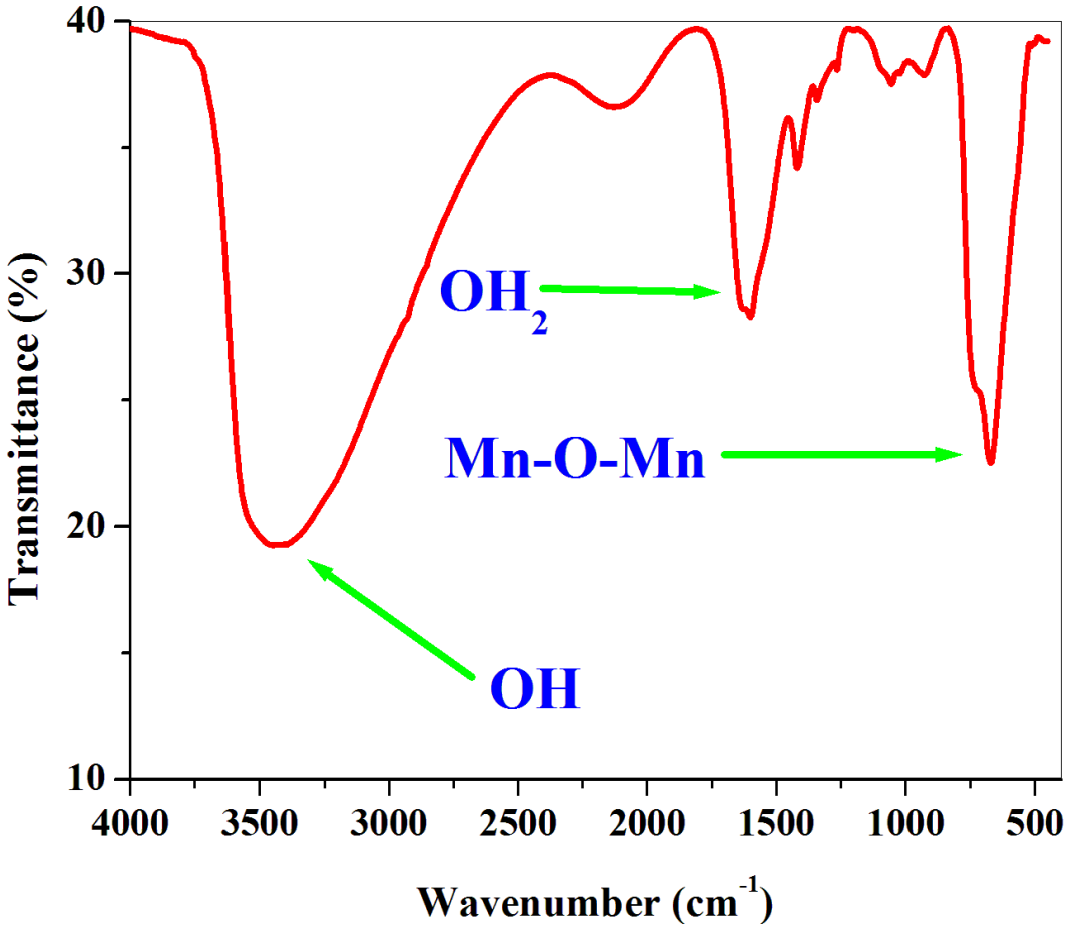


Fig. S3 Diffuse reflectance infrared Fourier transform spectrum of nanolayered Mn-K.

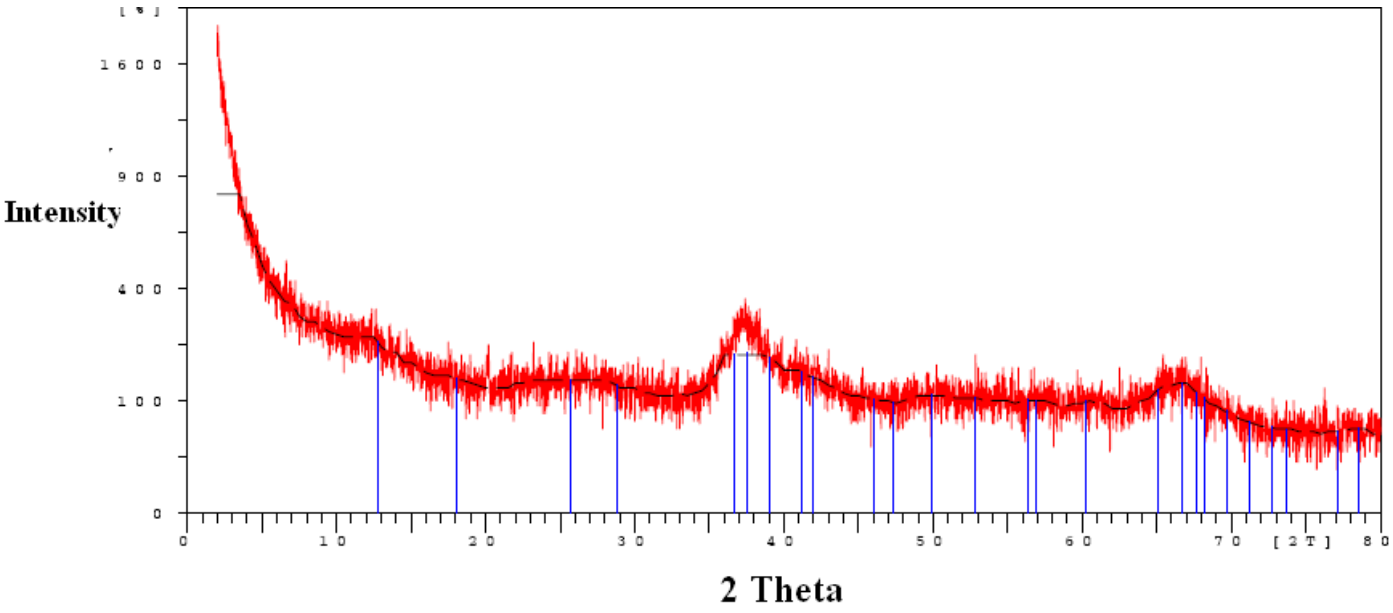


Fig. S4 XRD of nanolayered Mn-K prepared at 200 ^{o}C.

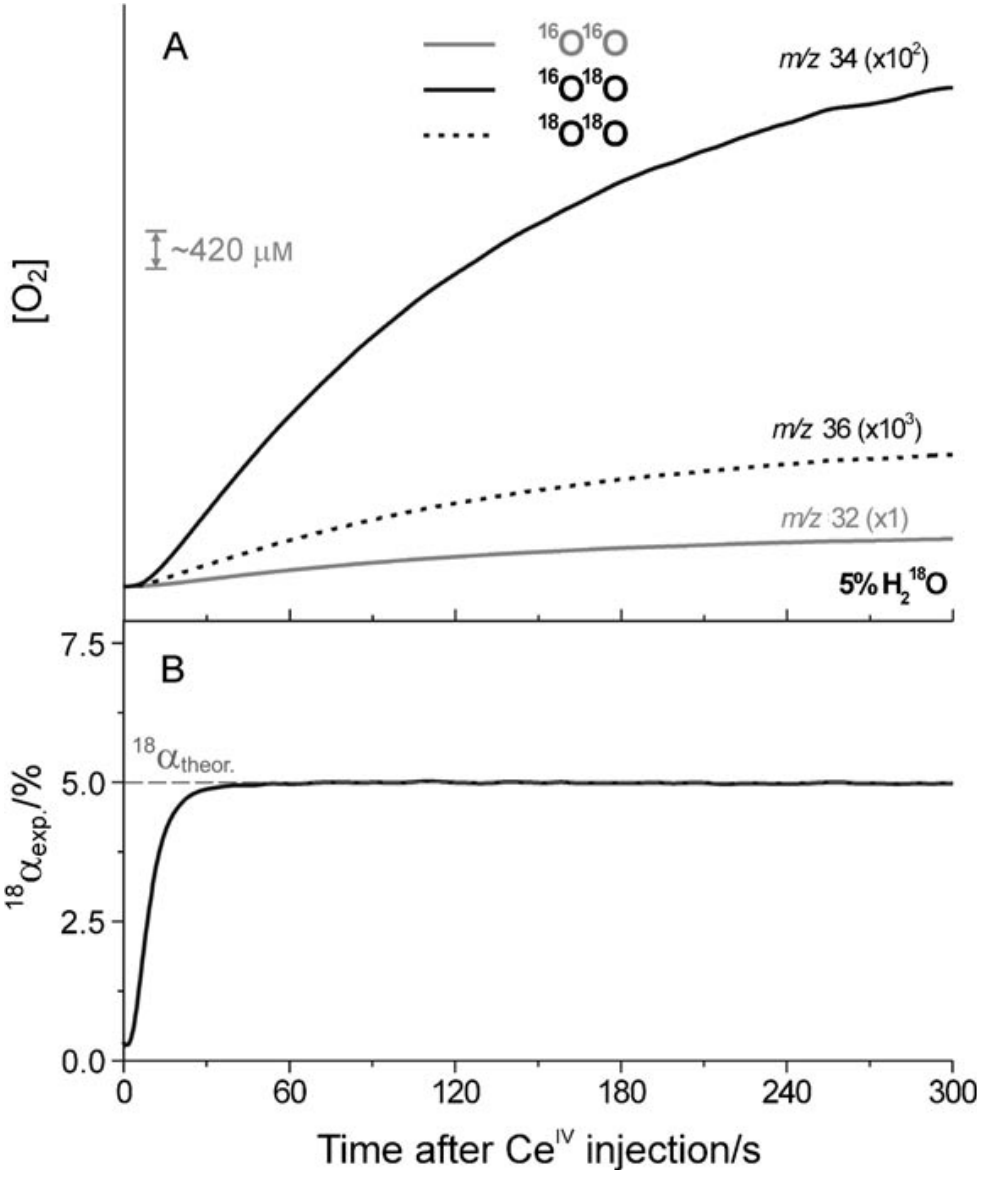


Fig. S5 A: Oxygen evolution traces for the reaction of layered Mn oxide with Ce(IV) detected by MIMS for $^{16}O_2$ (m/z: 32; solid grey trace), $^{16}O^{18}O$ (m/z: 34; solid black trace), and $^{18}O_2$ (m/z:36; black dashed trace). Ce(IV) in $H_2{}^{18}O$ enriched water was injected into the (non-enriched) oxide suspension at t = 0 s. Final oxide and Ce(IV) concentrations in the MIMS cell were 1 mgmL^{-1} and 100 mm, respectively. $H_2{}^{18}O$ enrichment of the reaction mixture: 5%. The absolute scale refers to an amplification factor of 1. B: Change in $^{18}\alpha$ value as a function of time calculated from the traces shown in A. Image and caption are from ref. S2.

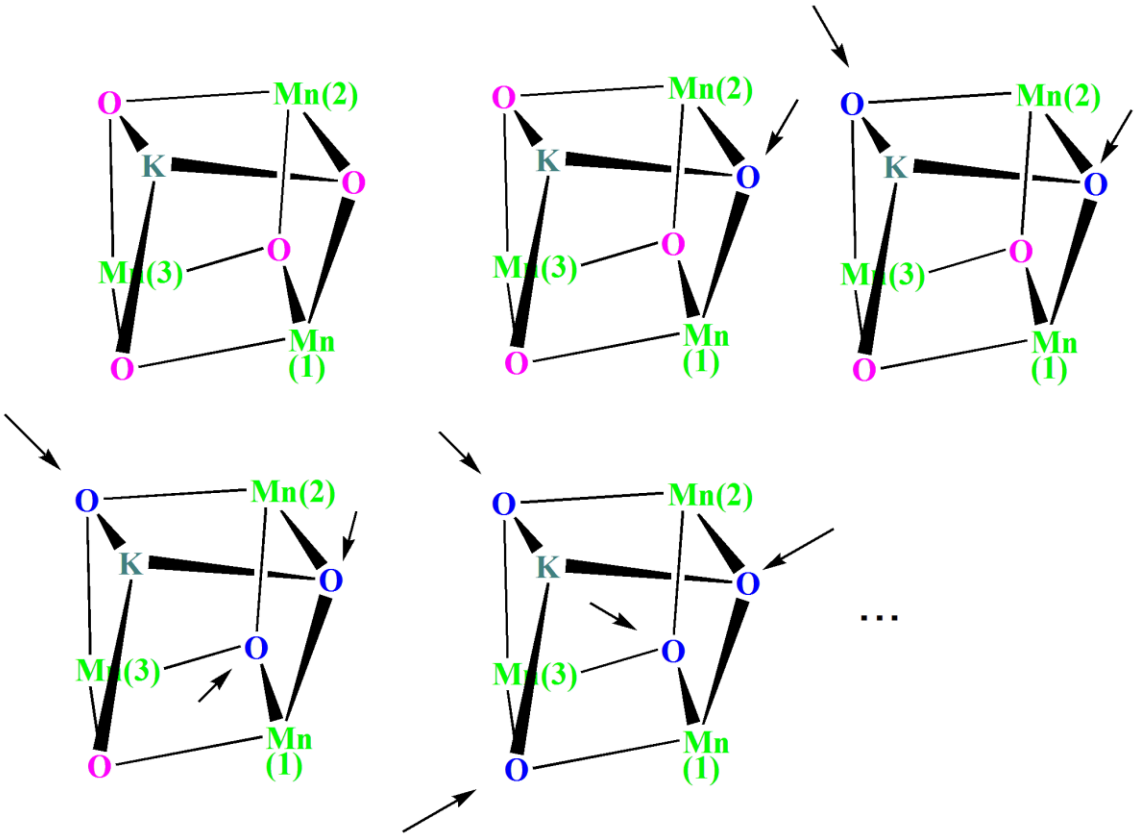


Fig. S6 Different motifs are formed by adding $H_2{}^{18}O$ to nanolayered Mn-K oxide. Each motif may different DRIFT peak in Mn-O-Mn area. Arrows show isotopic oxygen in the structure.

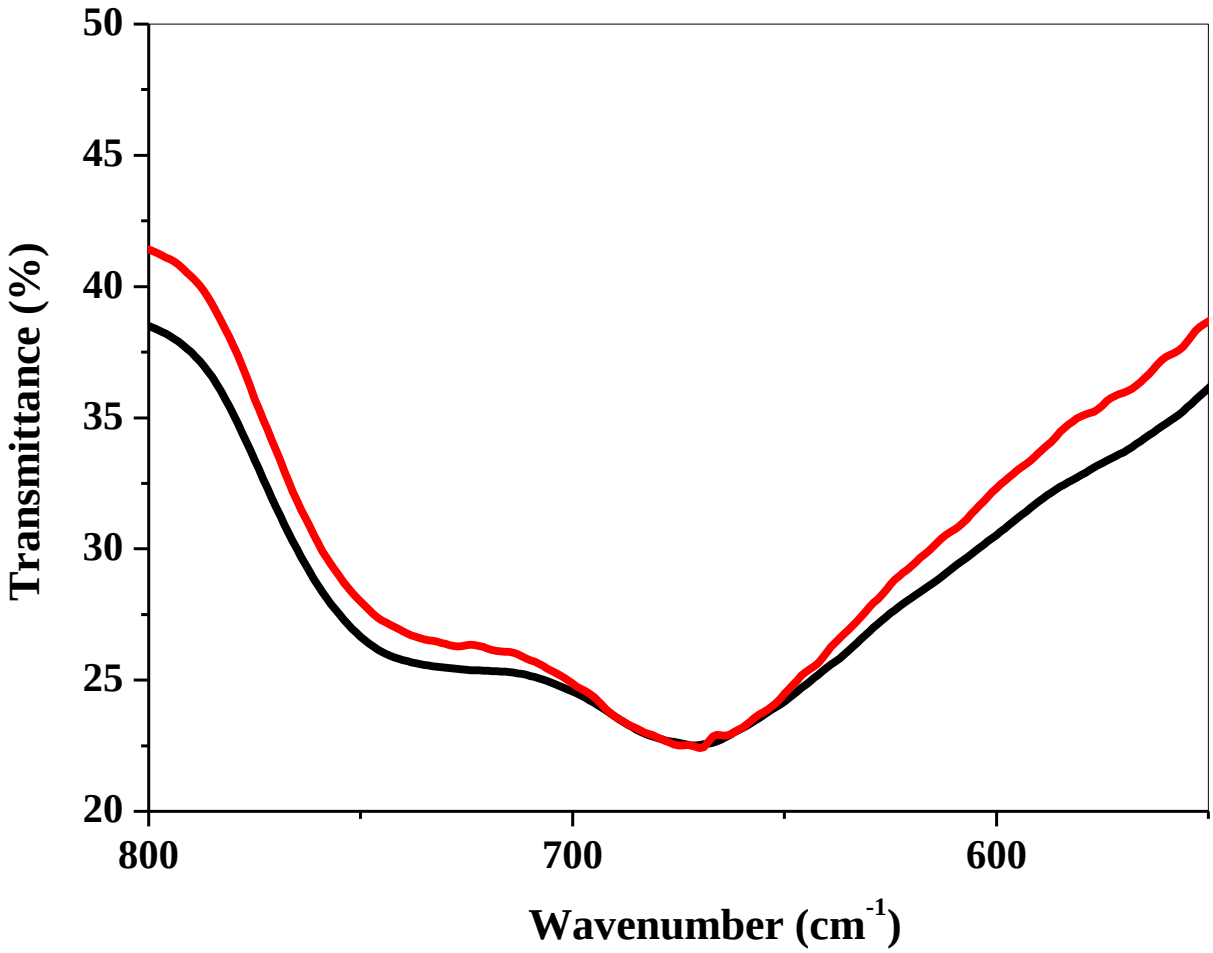


Fig. S7 DRIFT spectra of reference compound (black) and reference compound after 30 s (red).

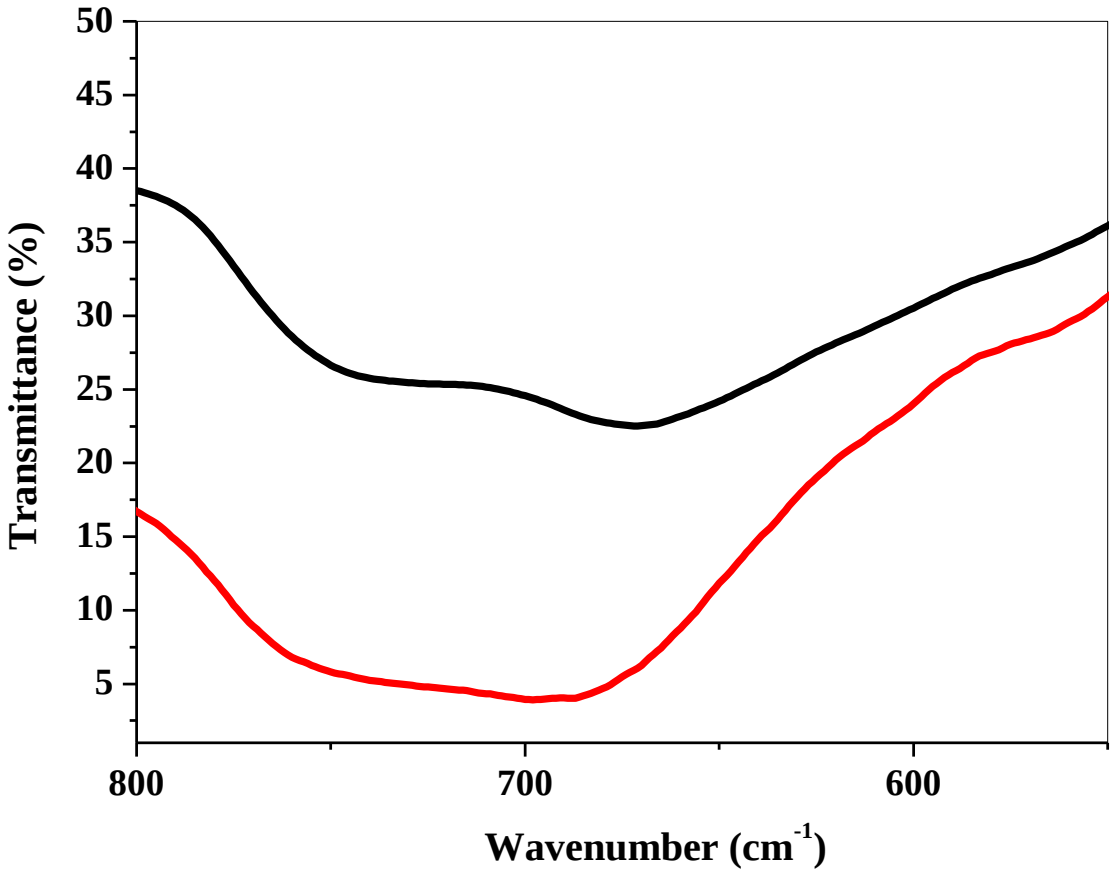


Fig. S8 DRIFT spectra of reference compound (black) and reference compound after 60 s (red).

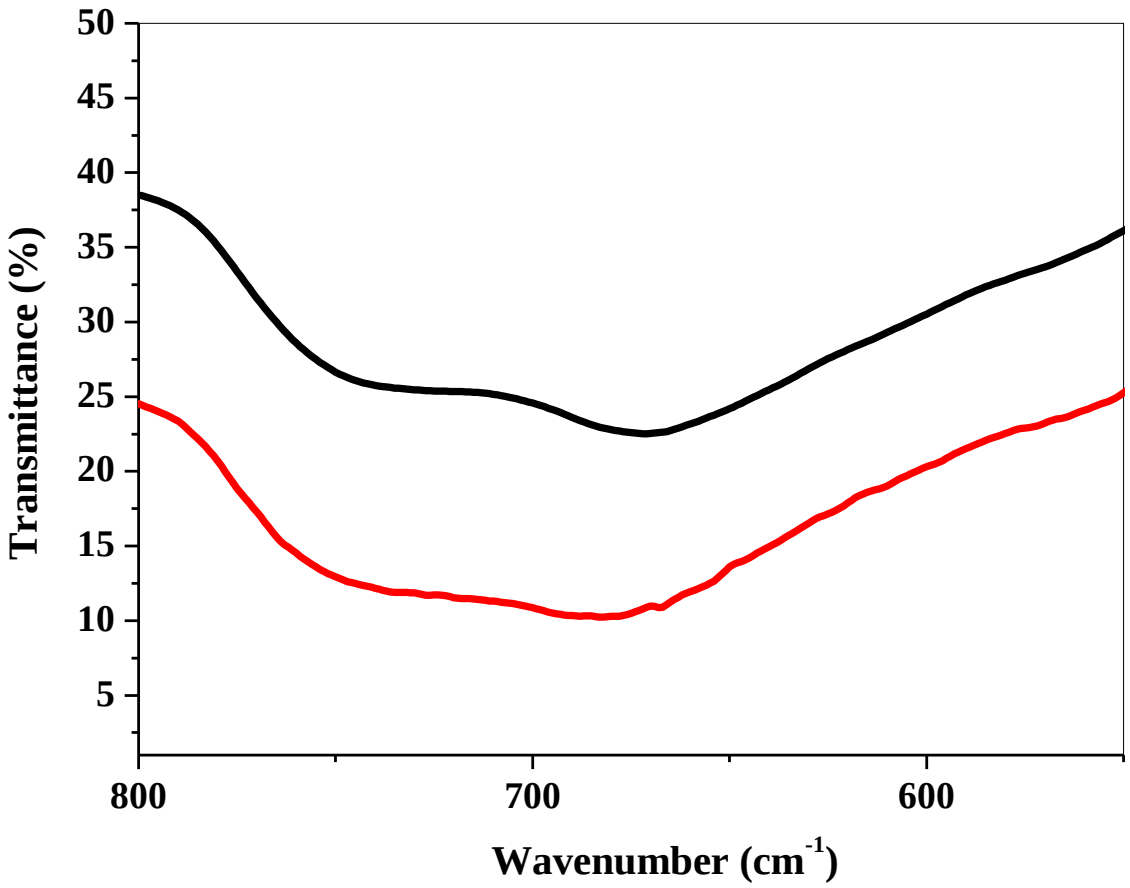


Fig. S8 DRIFT spectra of reference compound (black) and reference compound after 90 s (red).

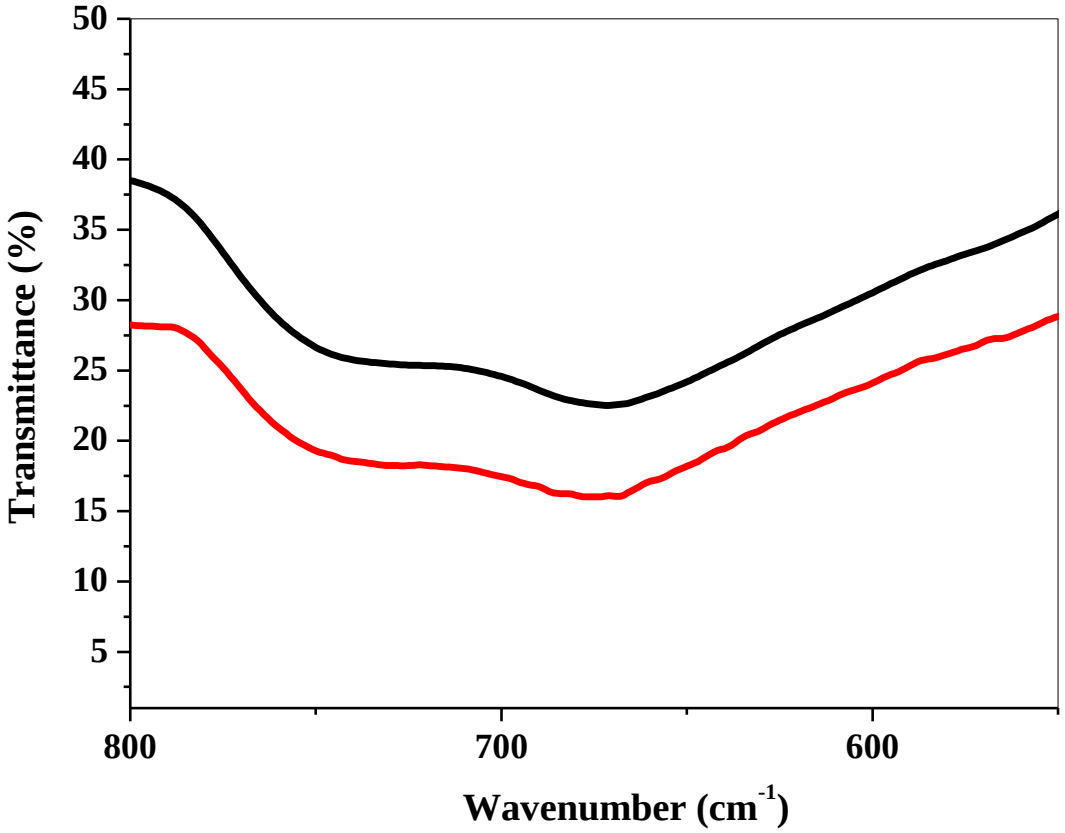


Fig. S9 DRIFT spectra of reference compound (black) and reference compound after 120 (red).

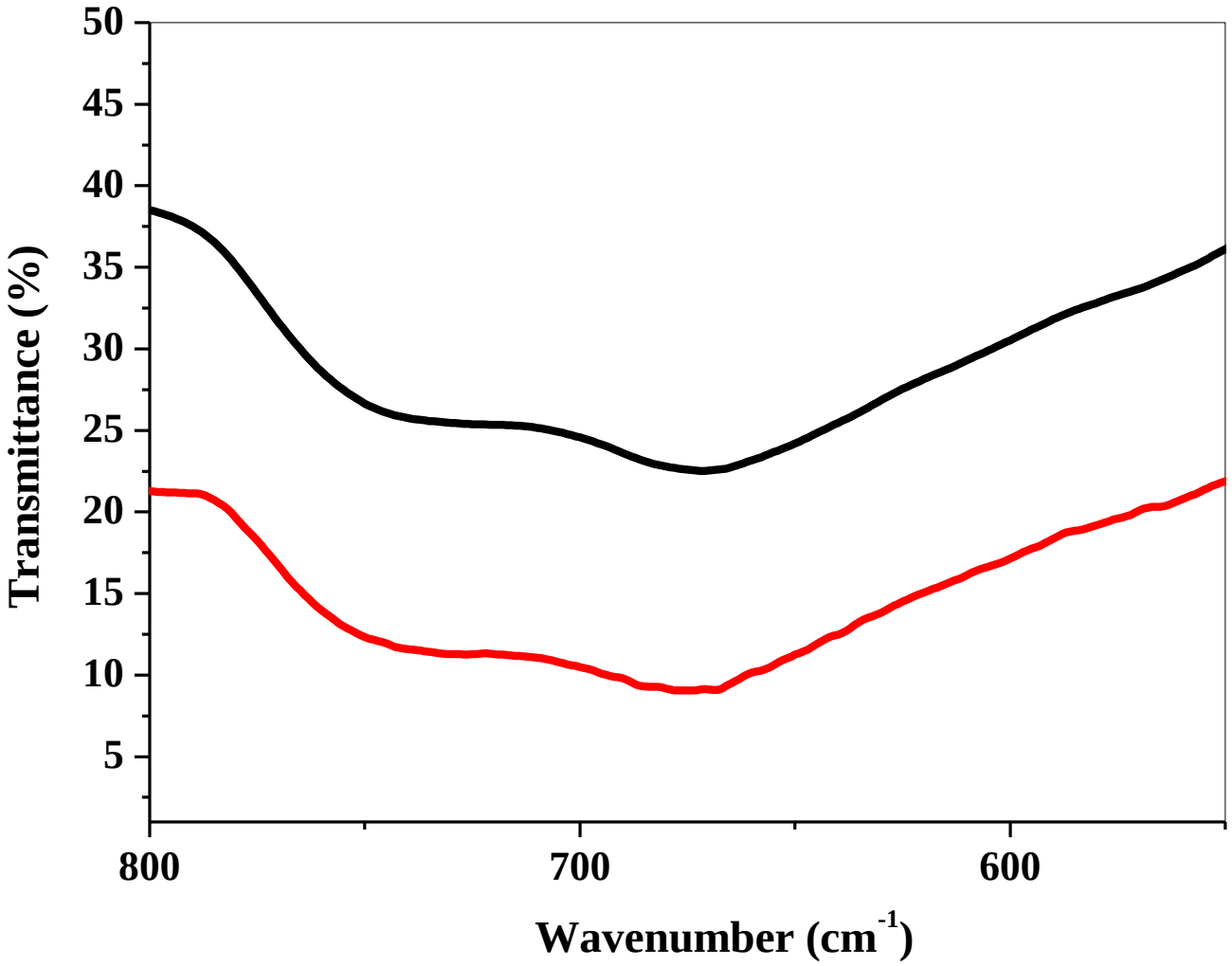


Fig. S10 DRIFT spectra of reference compound (black) and reference compound after 600 s (red).

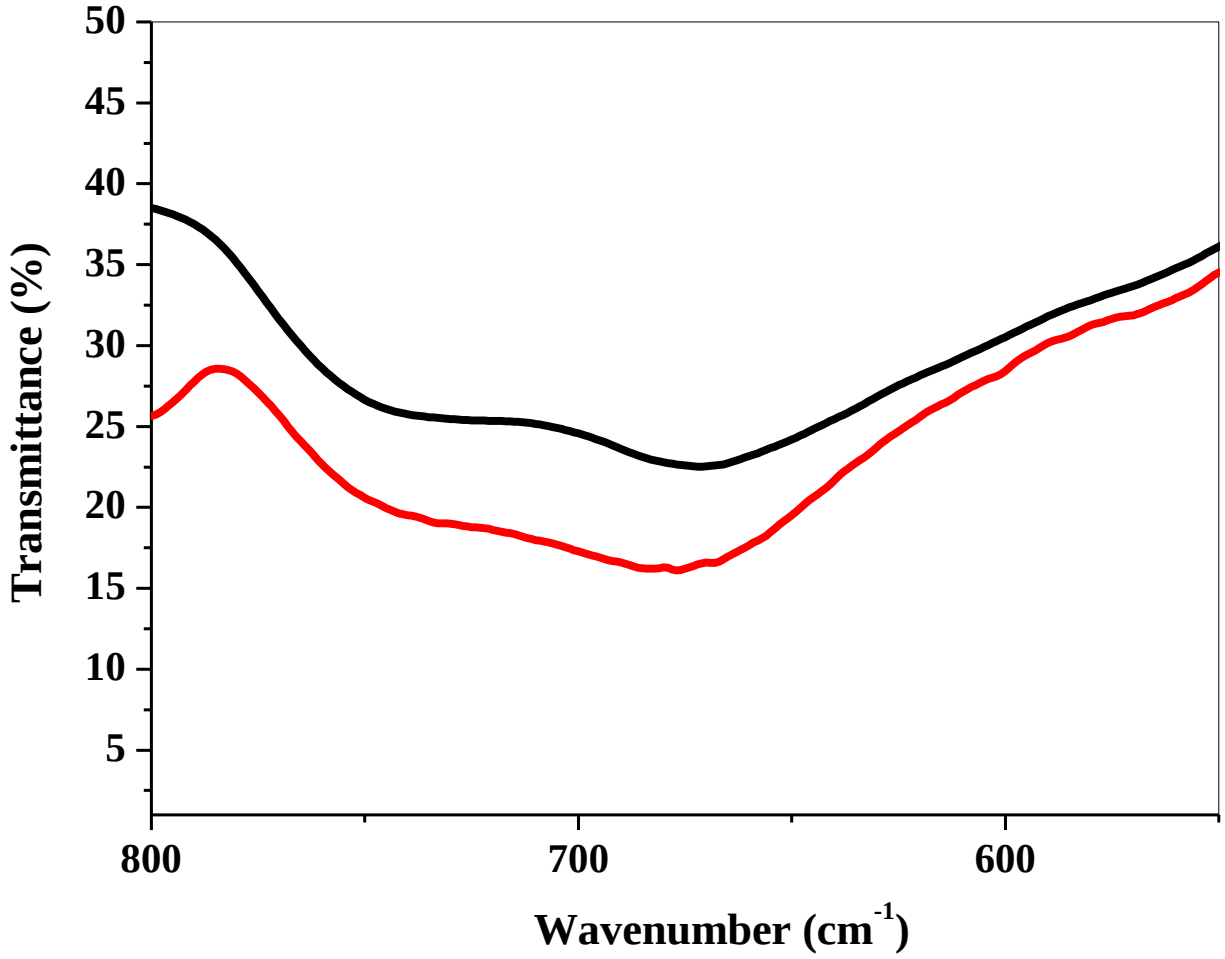


Fig. S11 DRIFT spectra of reference compound (black) and reference compound after 900 s (red).

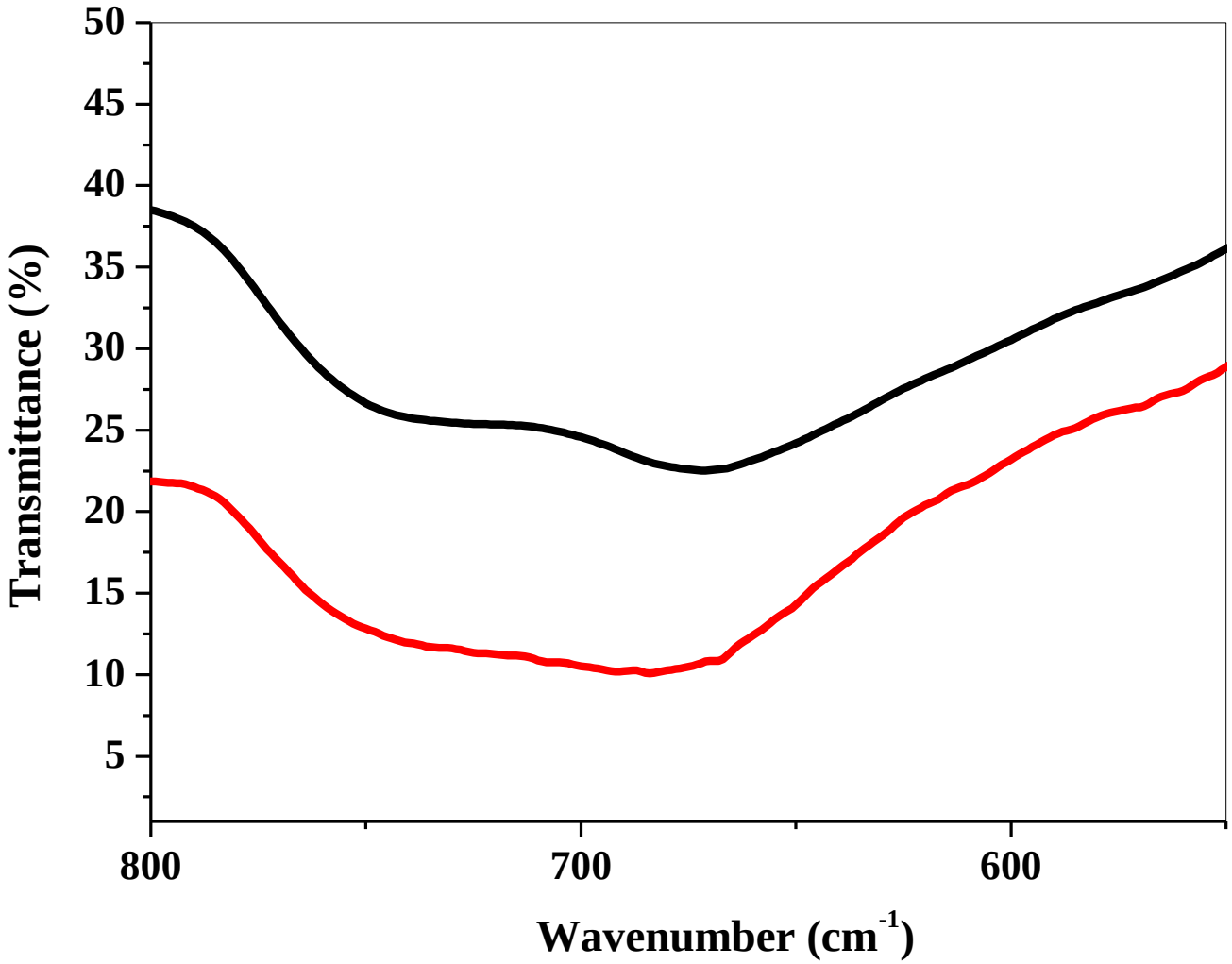


Fig. S12 DRIFT spectra of reference compound (black) and reference compound after 1800 s (red).

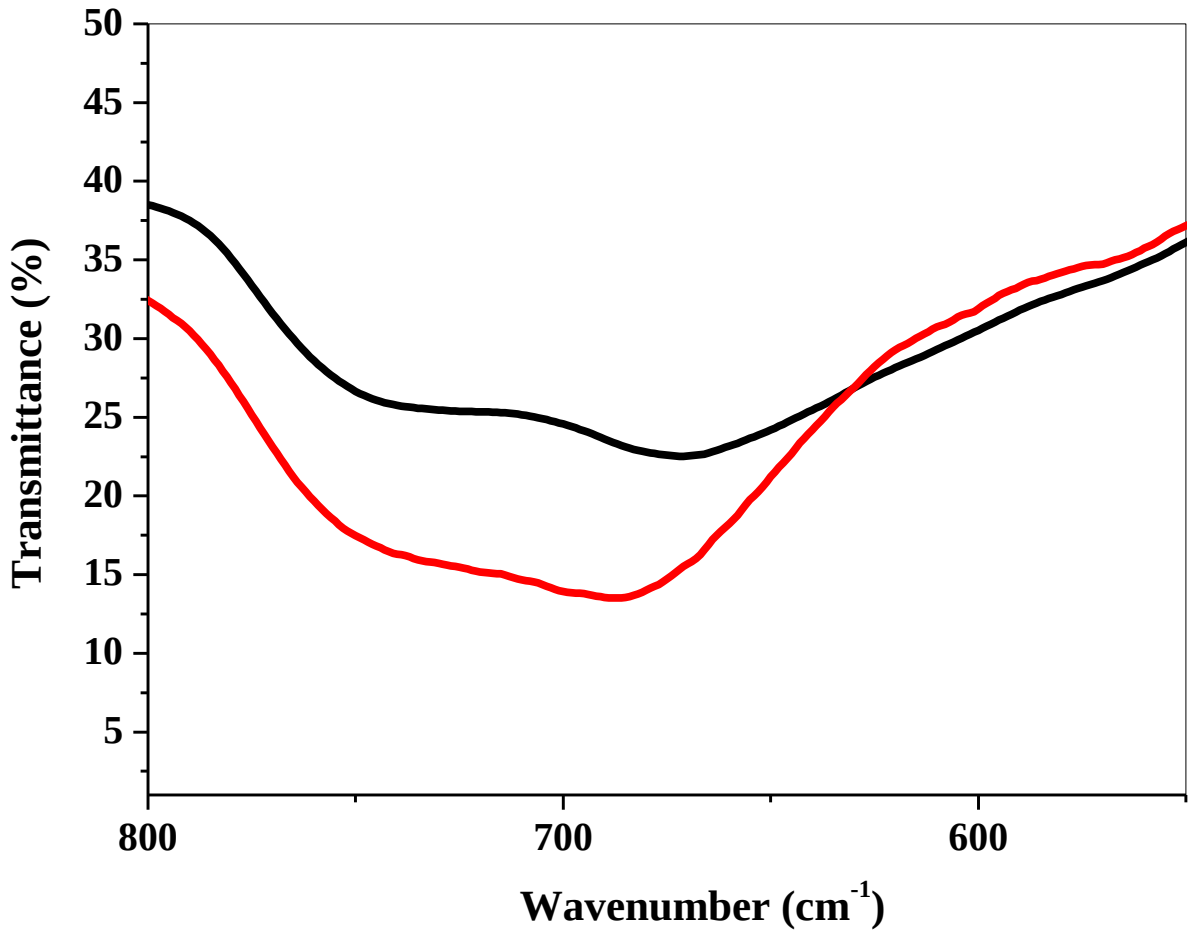


Fig. S13 DRIFT spectra of reference compound (black) and reference compound after 3 hours (red).

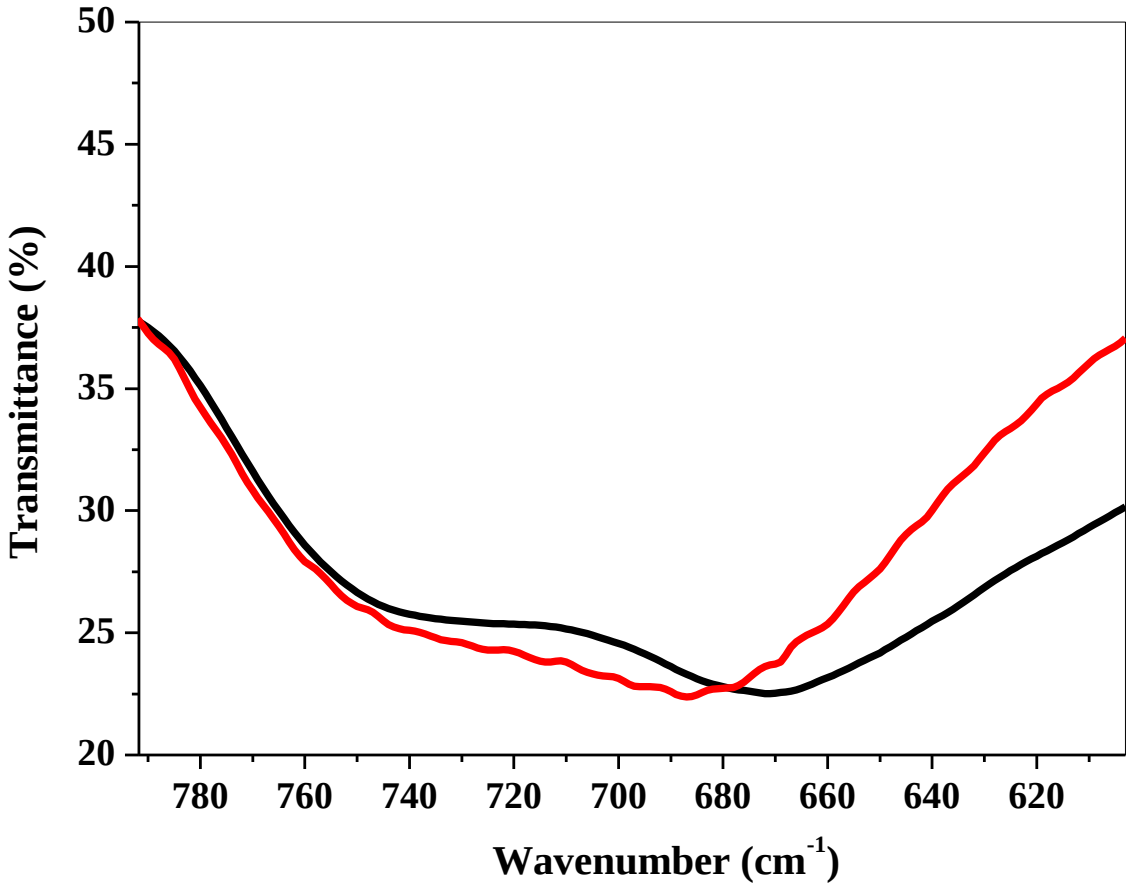


Fig. S13 DRIFT spectra of reference compound (black) and reference compound after 2 days (red).

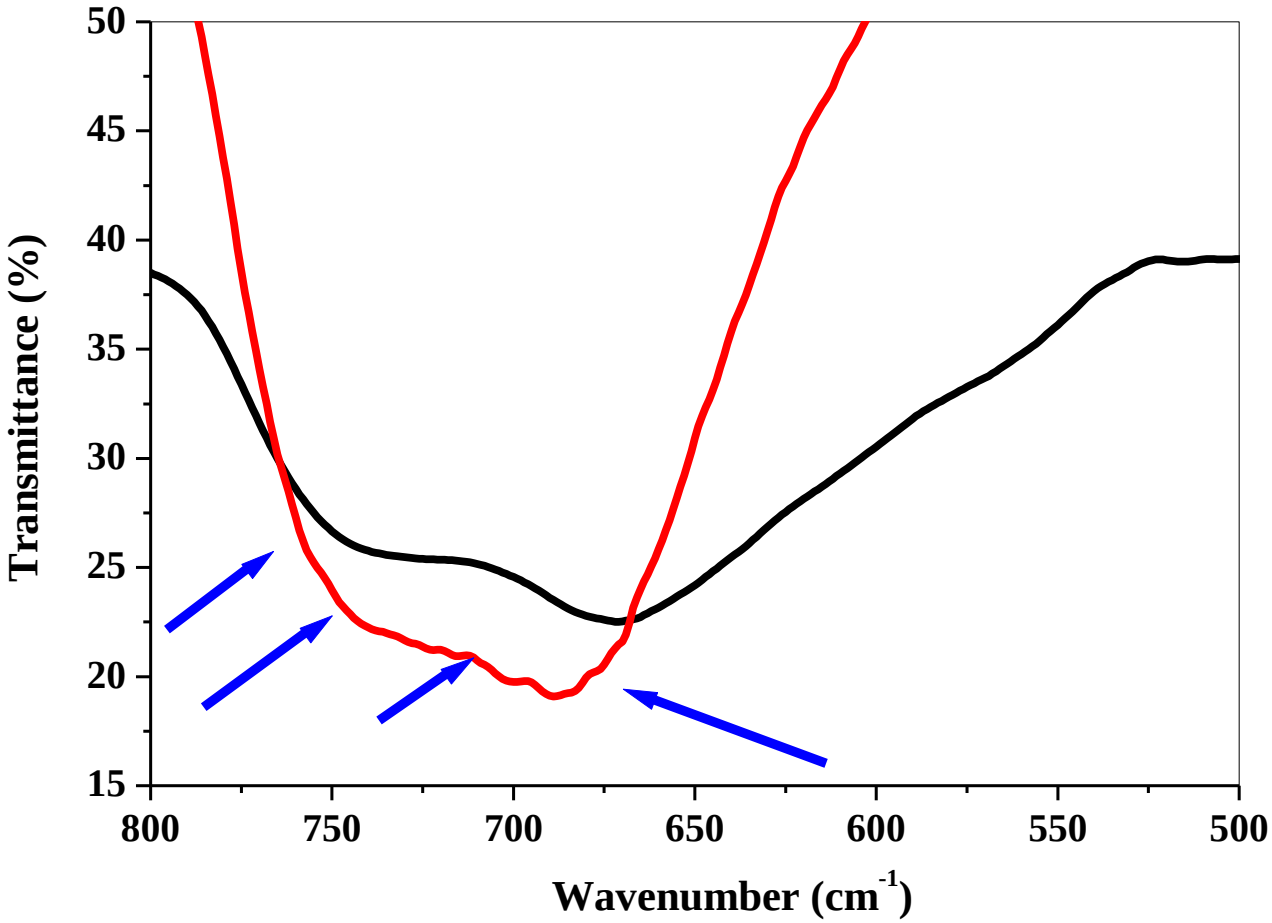


Fig. S14 DRIFT spectra of reference compound (black) and reference compound after one week (red). Blue arrows show new peaks related to ^{18}O in Mn oxide.

Table S1 Measured standard reduction potentials in aqueous solution (pH = 0) for water oxidation regarding different mechanisms (E_0 vs. SHE). Data are from ref. S3

Reaction	Standard E_0
Four-Electron Reactions	
$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$	1.229
$OH^- + H_2O \rightarrow O_2 + 3H^+ + 4e^-$	1.022
$2OH^- \rightarrow O_2 + 2H^+ + 4e^-$	0.815
$4OH^- \rightarrow O_2 + H_2O + 4e^-$	0.401
Two-Electron Reactions	
$2H_2O \rightarrow H_2O_2 + 2H^+ + 2e^-$	1.776
$2OH^- \rightarrow H_2O_2 + 2e^-$	0.948
$H_2O_2 \rightarrow O_2 + 2H^+ + 2e^-$	0.682
$H_2O_2 + 2OH^- \rightarrow O_2 + 2H_2O + 2e^-$	-0.146
One-Electron Reactions	
$H_2O \rightarrow OH + H^+ + e^-$	2.848
$OH^- \rightarrow OH + e^-$	2.020
$H_2O_2 \rightarrow HO_2 + H^+ + e^-$	1.495
$H_2O_2 + OH^- \rightarrow HO_2 + H_2O + e^-$	0.667
$HO_2 \rightarrow O_2 + H^+ + e^-$	-0.130
$HO_2 + OH^- \rightarrow O_2 + H_2O + e^-$	-0.958

References

S1 M. M. Najafpour, D. Jafarian Sedigh, B. Pashaei and S. Nayeri, *New J. Chem*., 2013, **37**, 2448.

S2 D. Shevela, S. Koroidov, M. M. Najafpour, J. Messinger and P. Kurz, *Chem. Eur. J*., 2011, **17**, 5415.

S3 W. Ruettinger and G. C. Dismukes, *Chem. Rev*., 1997, **97**, 1.