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Electronic Supplementary Information

Nanosized Mn oxide/boron nitride composite as a catalyst for water oxidation

Mohammad Mahdi Najafpour,[*ab] Sepideh Madadkhani,[a] Tatsuya Tomo[c] and Suleyman I. Allakhverdiev[*d-f]

[a]Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

[b]Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran

[c]Department of Biology, Faculty of Science, Tokyo University of Science, Kagurazaka 1-3, Shinjuku-ku, Tokyo 162-8601, Japan

[d]Controlled Photobiosynthesis Laboratory, Institute of Plant Physiology, Russian Academy of Sciences, Botanicheskaya Street 35, Moscow 127276, Russia

[e]Institute of Basic Biological Problems, Russian Academy of Sciences, Pushchino, Moscow Region 142290, Russia

[f] Department of Plant Physiology, Faculty of Biology, M.V. Lomonosov Moscow State University, Leninskie Gory 1-12, Moscow 119991, Russia

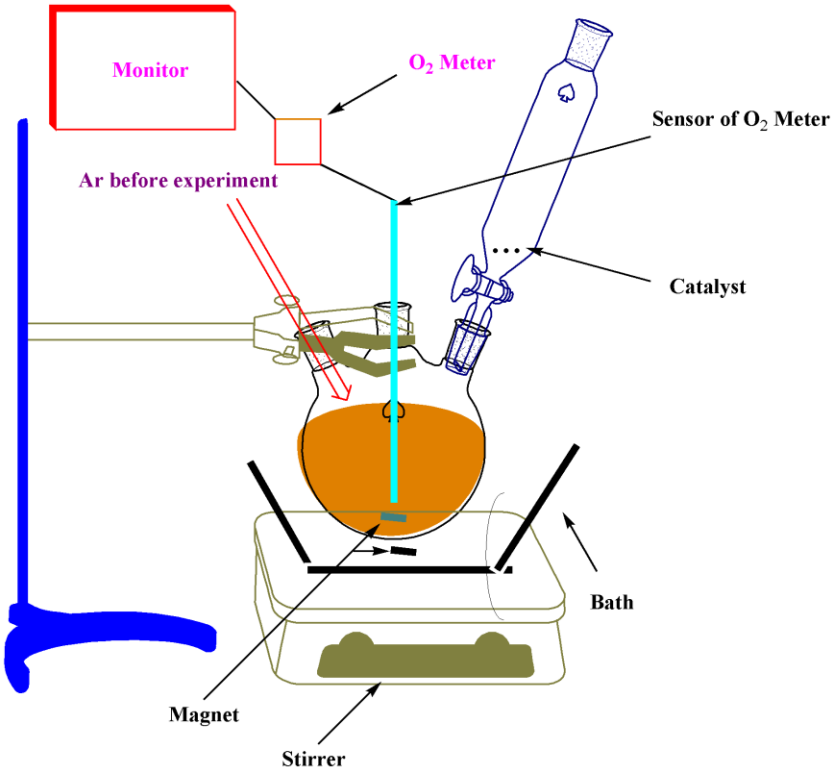
*Corresponding authors; Phone: (+98) 24 3315 3201; E-mail: mmnajafpour@iasbs.ac.ir; Phone: (+7) 496 773 1837; Fax: (+7) 496 7330 532; E-mail: suleyman.allakhverdiev@gmail.com

Water oxidation

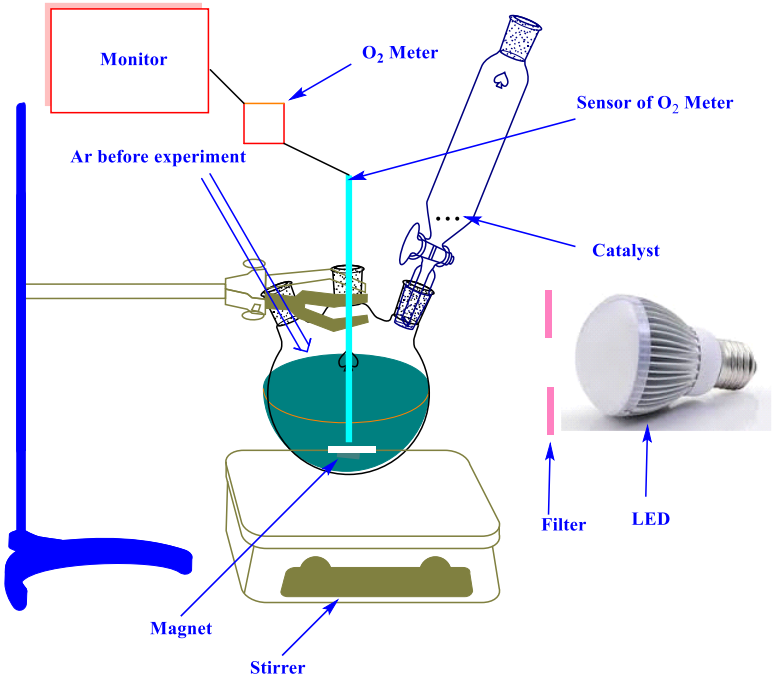
Oxygen evolution from aqueous solutions in the presence of cerium(IV) ammonium nitrate (Ce(IV)) at 25 ºC was investigated using a HQ40d portable dissolved oxygen-meter connected to an oxygen monitor with digital readout. In a typical run, the instrument readout was calibrated against air-saturated distilled water stirred continuously with a magnetic stirrer in the air-tight reactor. After ensuring a constant baseline reading, water in the reactor was replaced with Ce(IV) solution. Without the catalyst, Ce(IV) was stable, and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, the catalyst as a powder was added, and oxygen evolution was recorded with the oxygen meter under stirring (Scheme S1a). The formation of oxygen was followed, and the oxygen formation rates per Mn site were obtained from linear fits of the data by the initial rate.

Water Oxidation in the presence of $Ru(bpy)_3^{2+}$

Photochemical water oxidation experiments were performed in a 100 mL flask containing 80 mL of aqueous buffer (Na_2SiF_6-$NaHCO_3$, 0.028 M) with pH held at 5.8, Na_2SO_4 (300.0 mg), $Na_2S_2O_8$ (1300.0 mg), $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ (7.0 mg), and the catalyst (200.0 mg). After deaeration of the solution with Ar, the reactor was irradiated with a white LED (100 W) in a home-made device and the oxygen formation was recorded by a using an HQ40d portable dissolved oxygen-meter connected to an oxygen monitor with digital readout. A longpass filters (> 400 nm) from Thorlabs Company (USA) was used as a light filter (Scheme S1b).



a



b

Scheme S1 Setup for water-oxidation reaction in the presence of Ce(IV) (a) and photochemical produced $Ru(bpy)_3^{3+}$ (b).

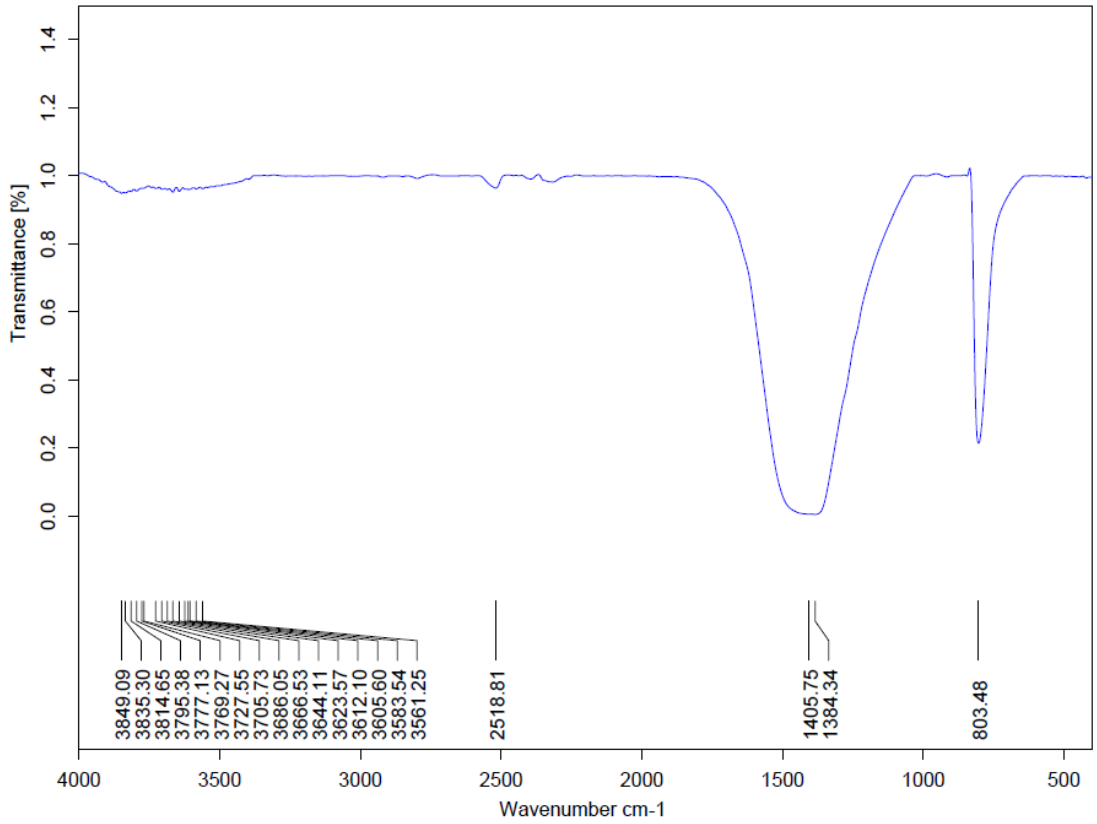


Figure S1 FTIR spectrum of BN.

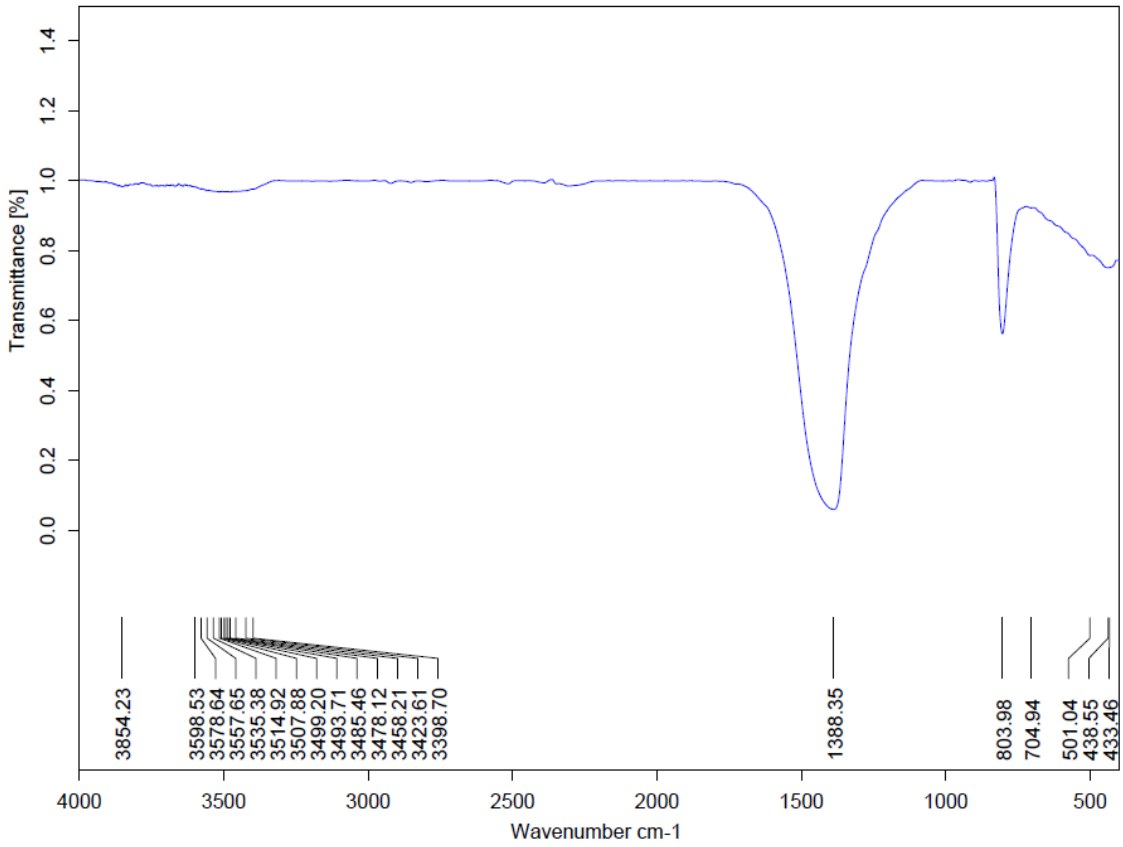


Figure S2 FTIR spectrum of calcined Mn oxide/BN at 60 °C.

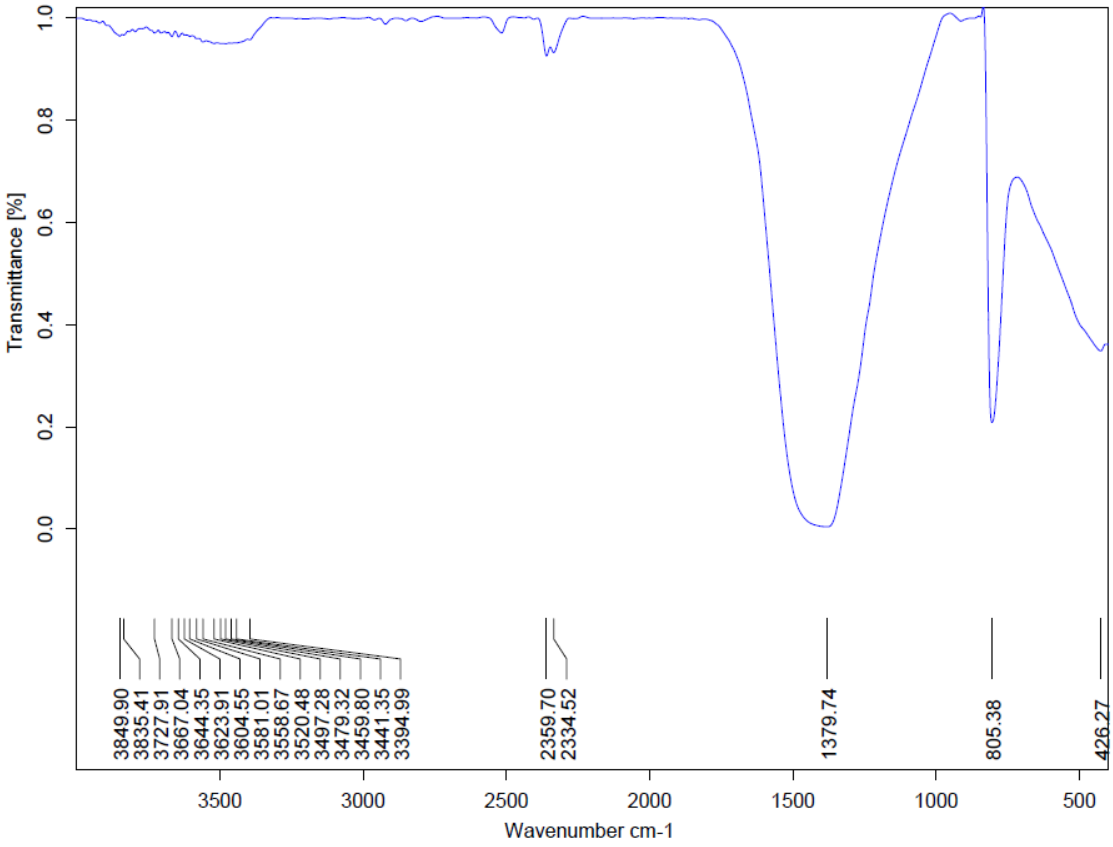


Figure S3 FTIR spectrum of calcined Mn oxide/BN oxides at 100 °C.

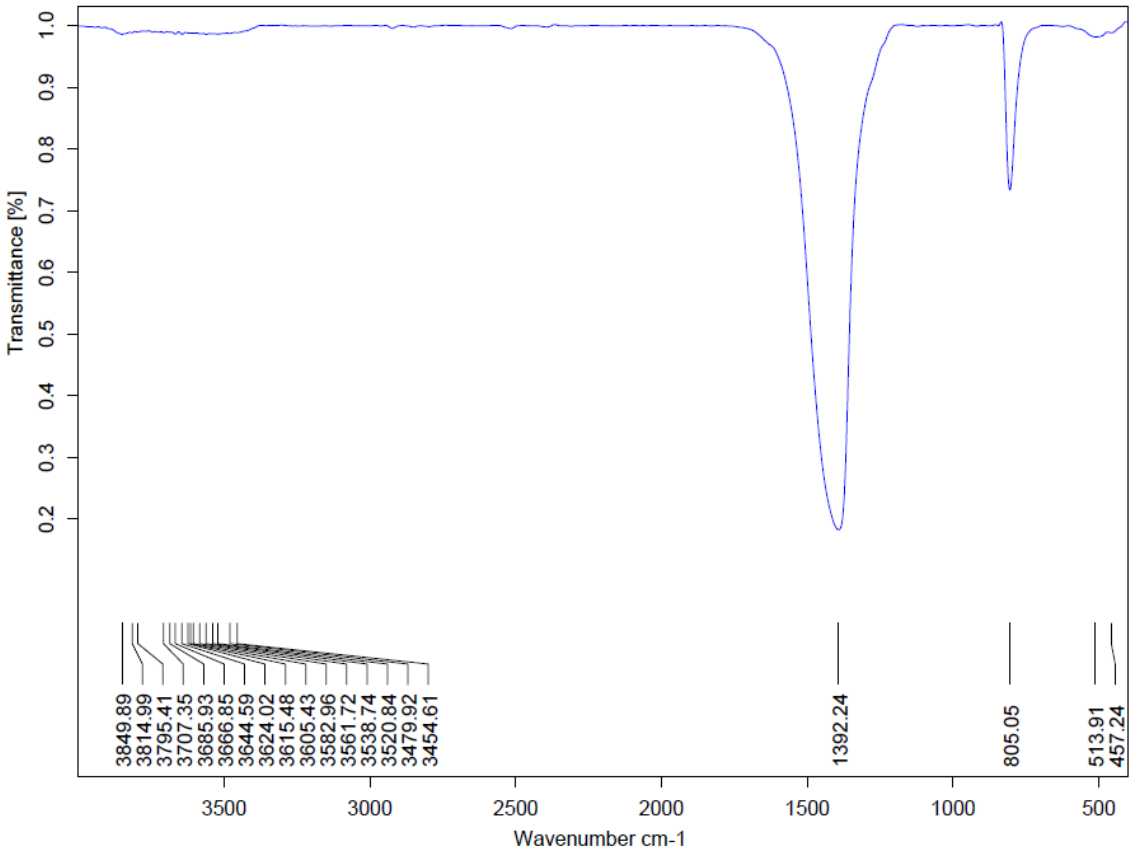


Figure S4 FTIR spectrum of calcined Mn oxide/BN at 200 ℃.

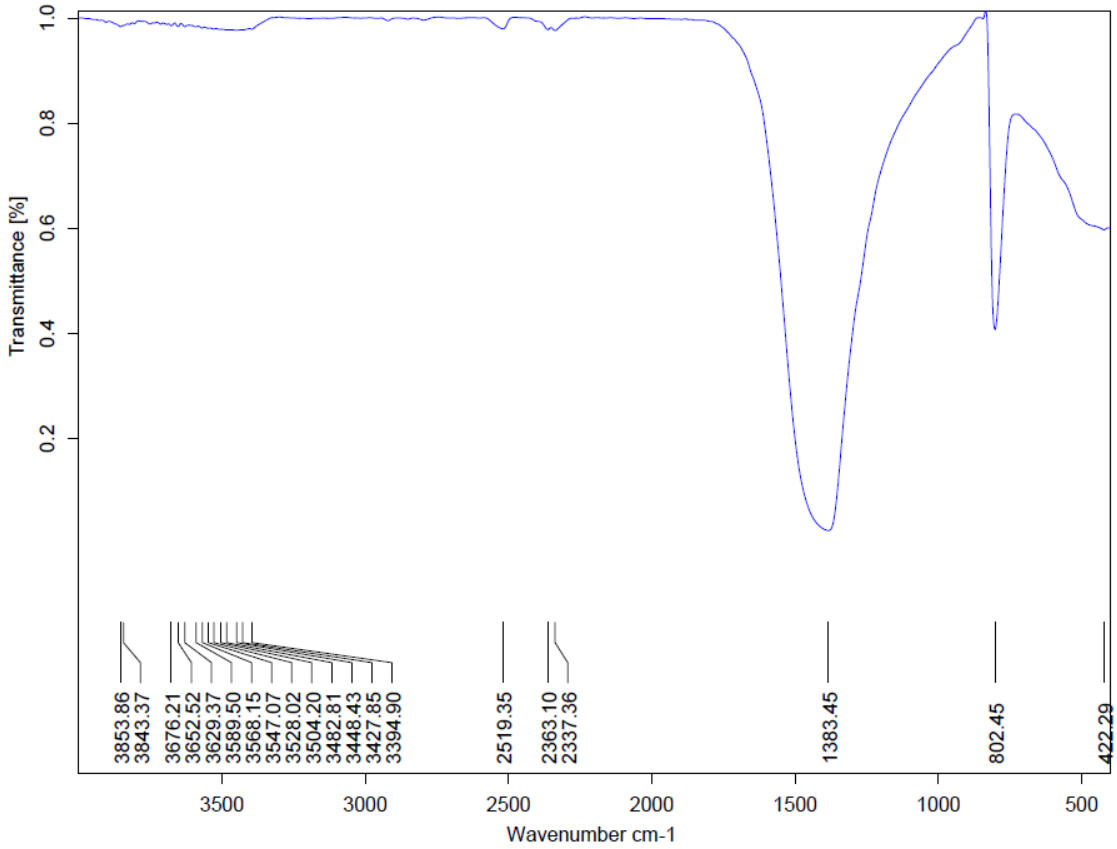


Figure S5 FTIR spectrum of calcined Mn oxide/BN at 300 °C.

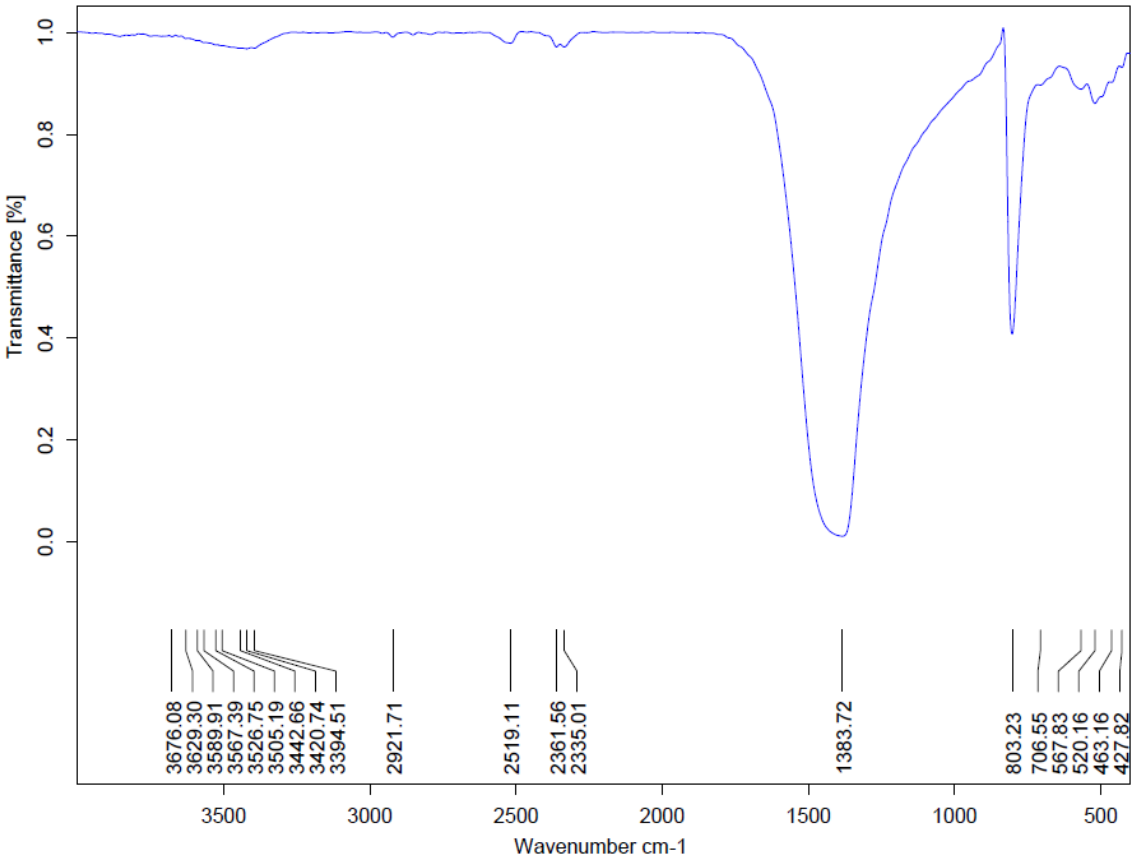


Figure S6 FTIR spectrum of calcined Mn oxide/BN at 400 ℃.

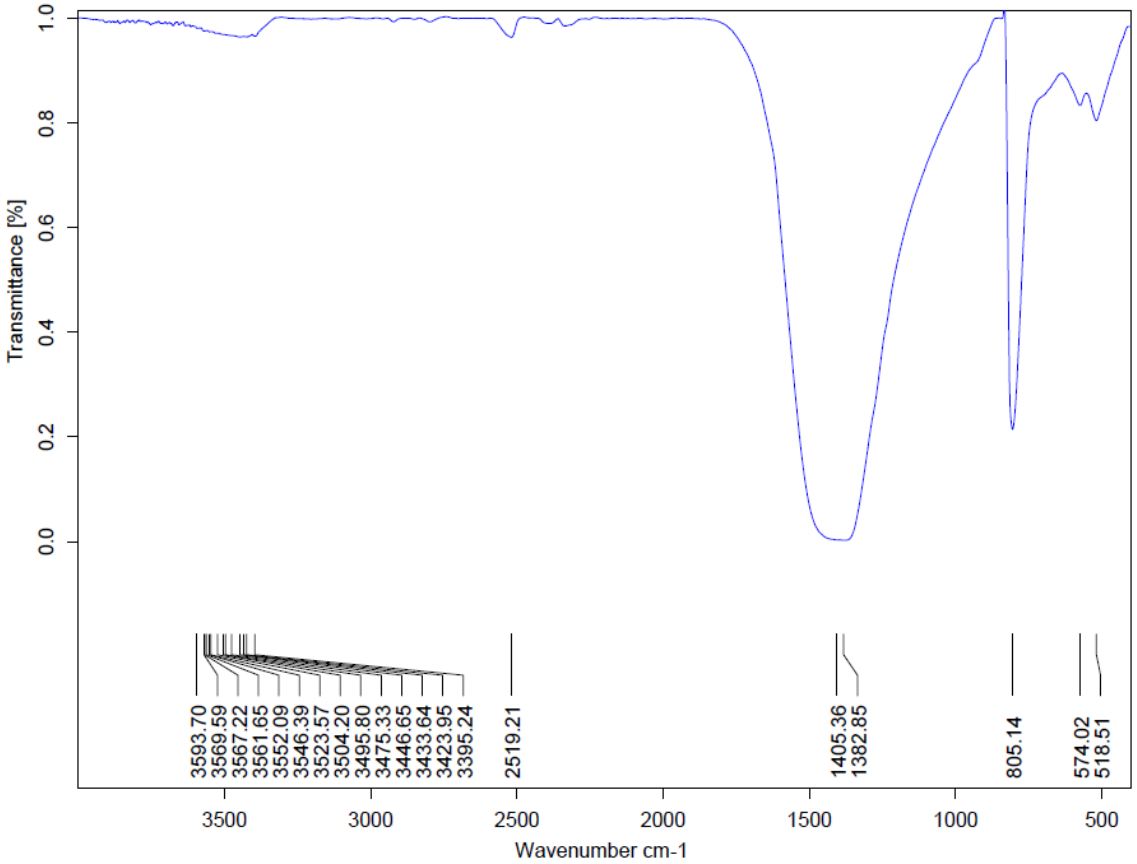


Figure S7 FTIR spectrum of calcined Mn oxide/BN at 500 ℃.

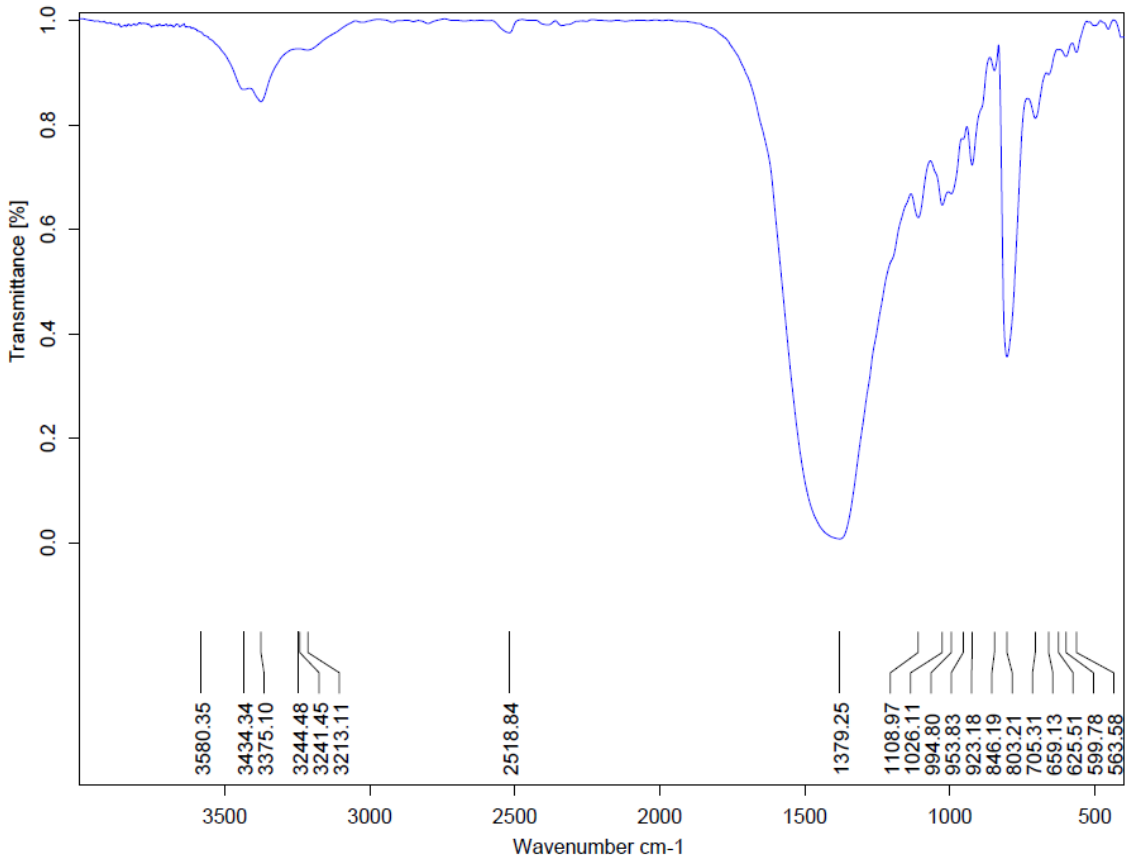


Figure S8 FTIR spectrum of calcined Mn oxide/BN at 600 ℃.

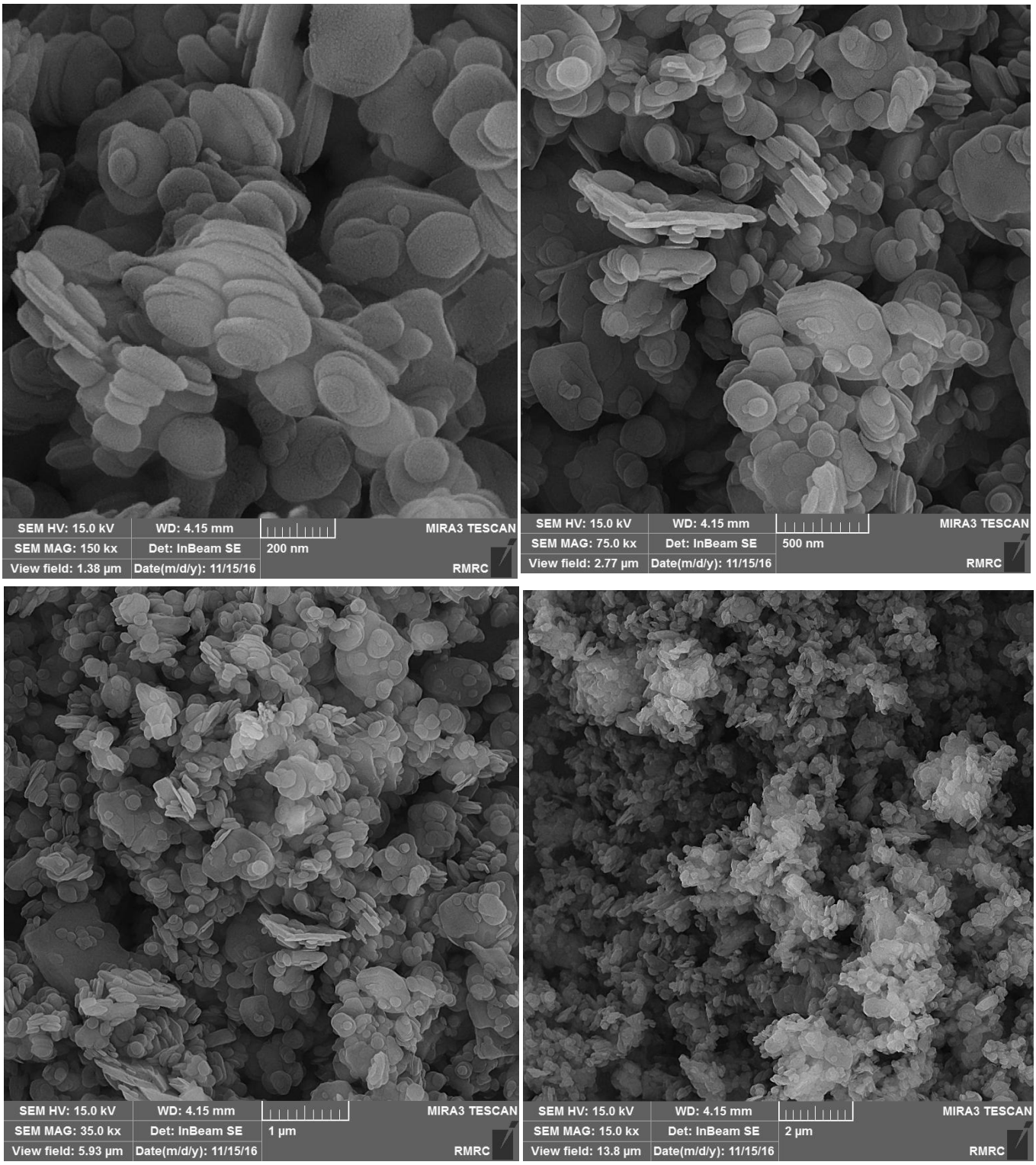


Figure S9 SEM images of BN.

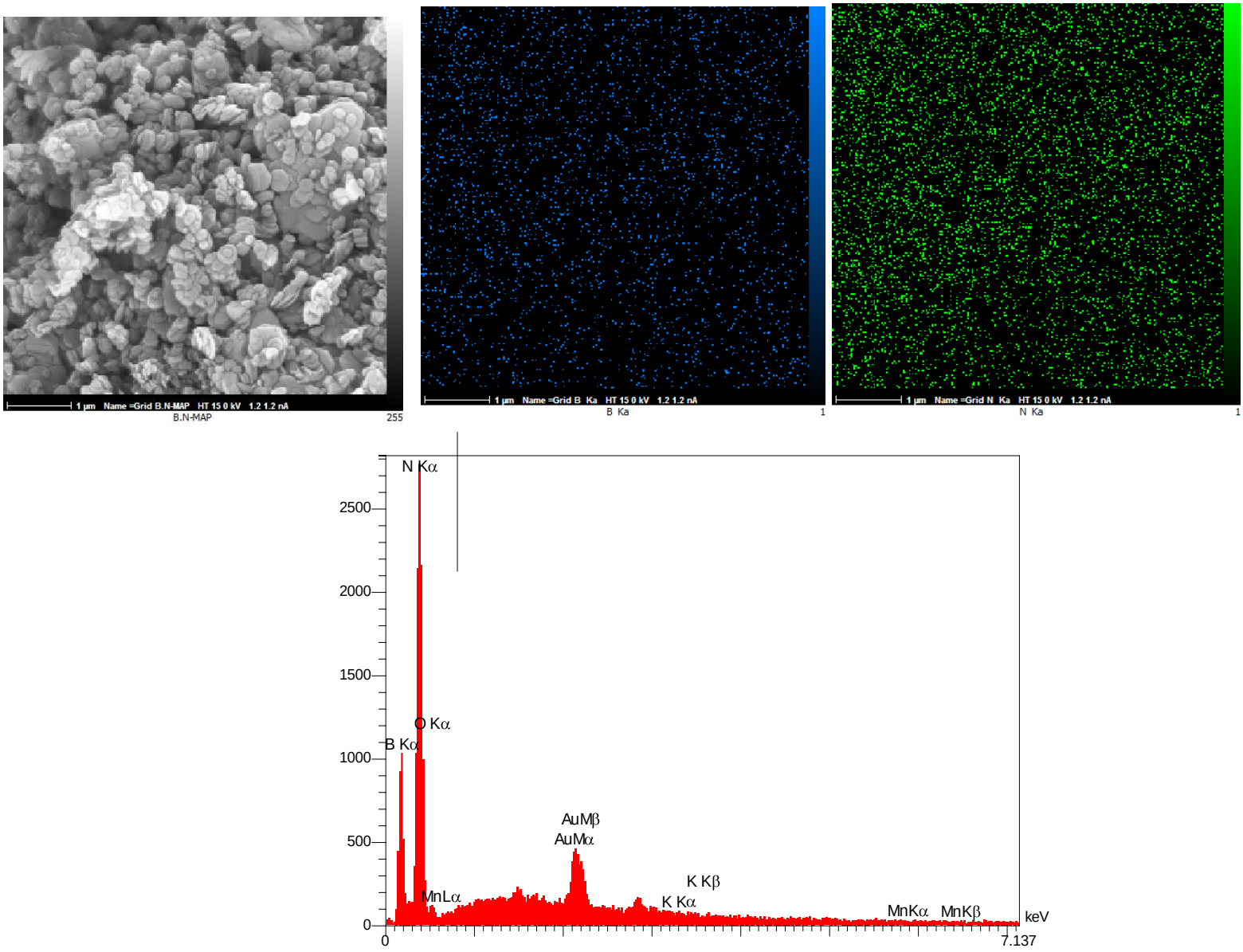


Figure S10 EDX-Mapping for BN (B: blue and N: green).

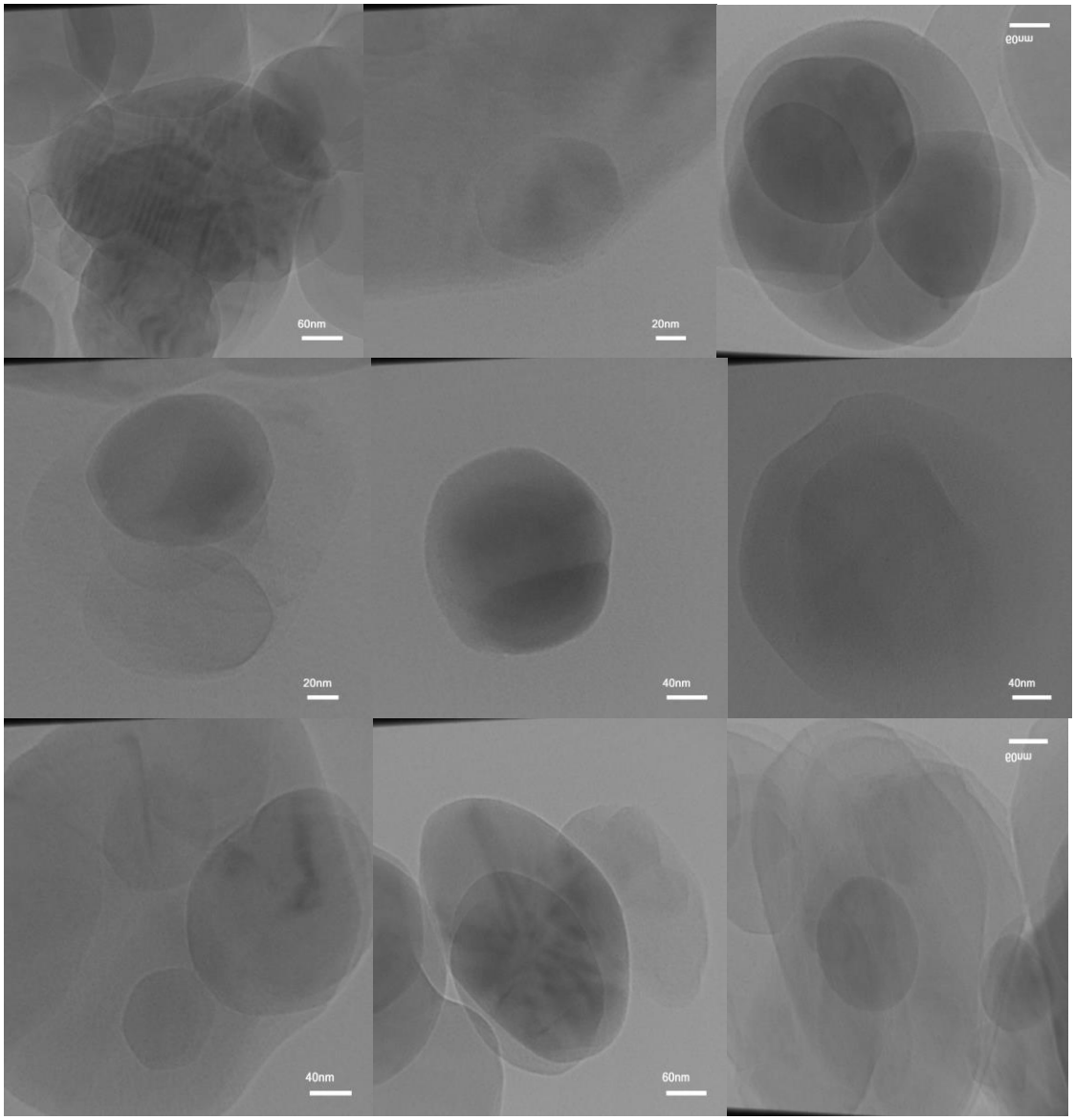


Figure S11. TEM images of BN.

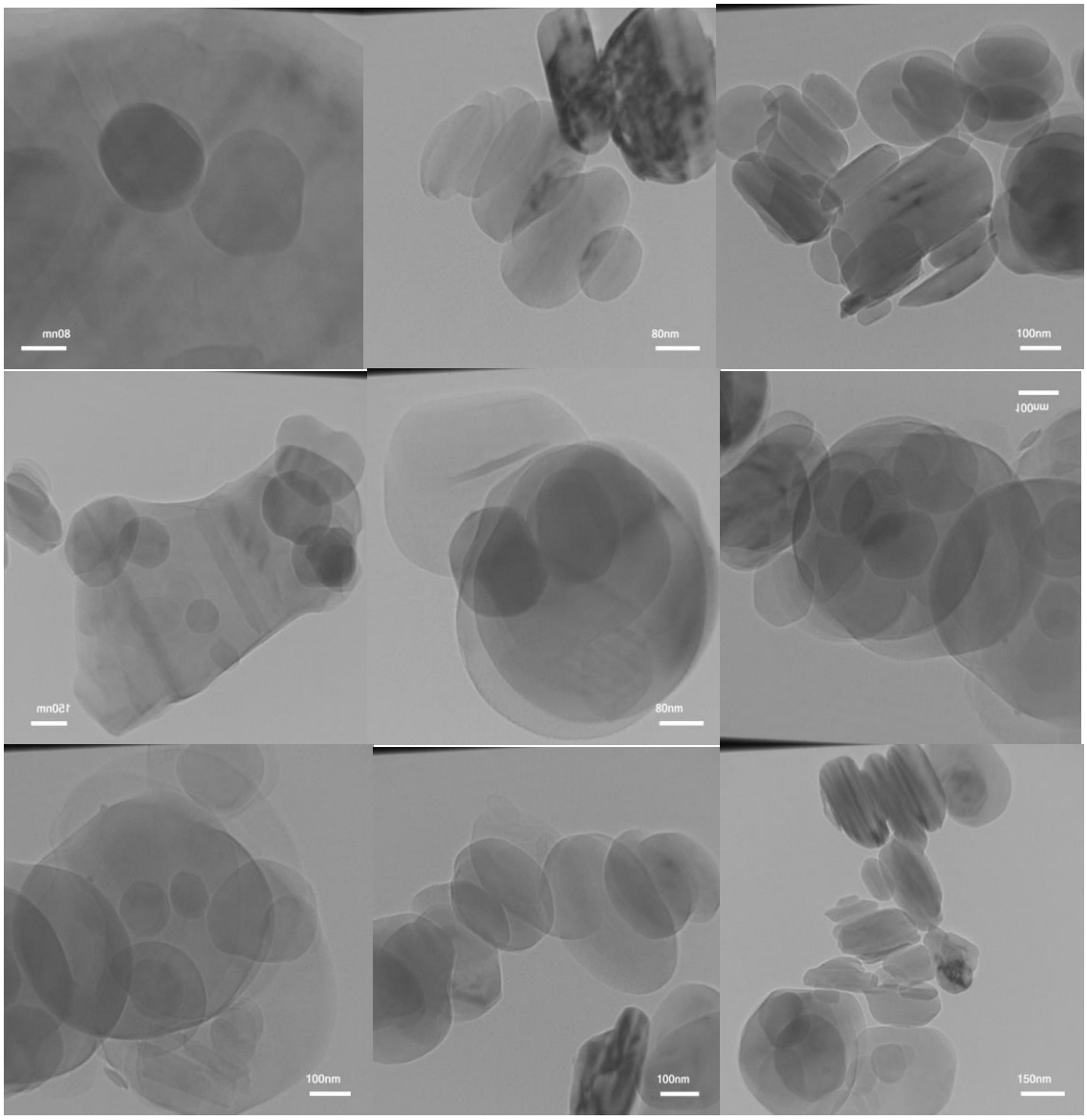


Figure S12. TEM images of BN.

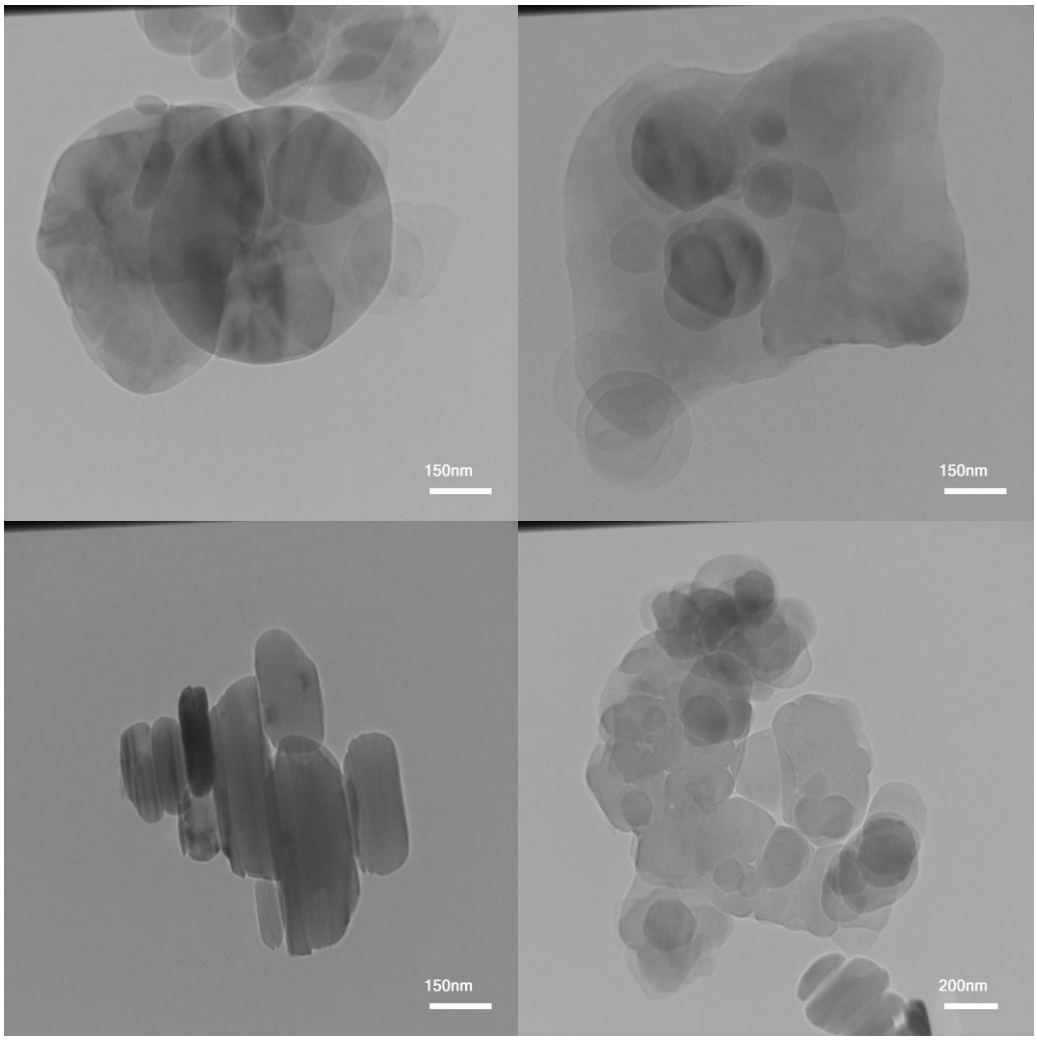


Figure S13. TEM images of BN.

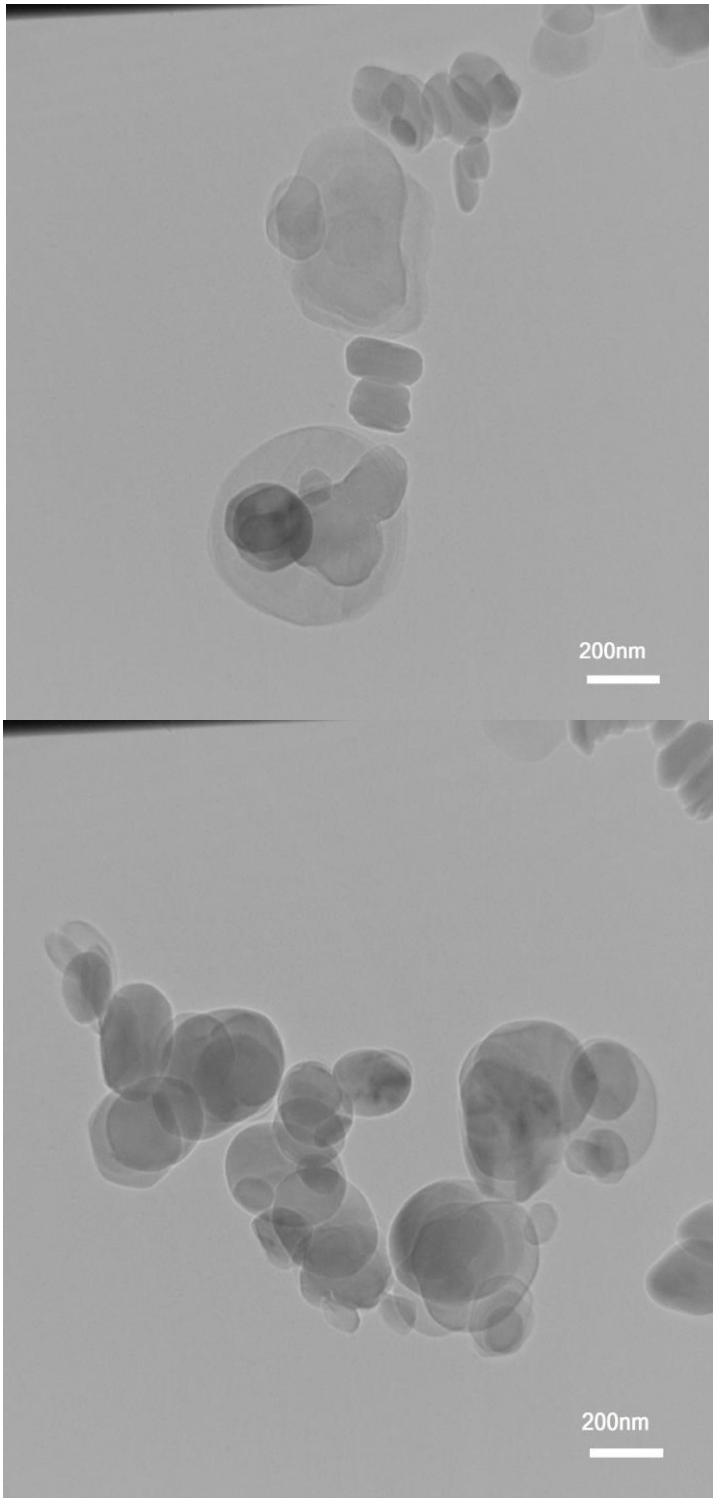


Figure S14. TEM images of BN.

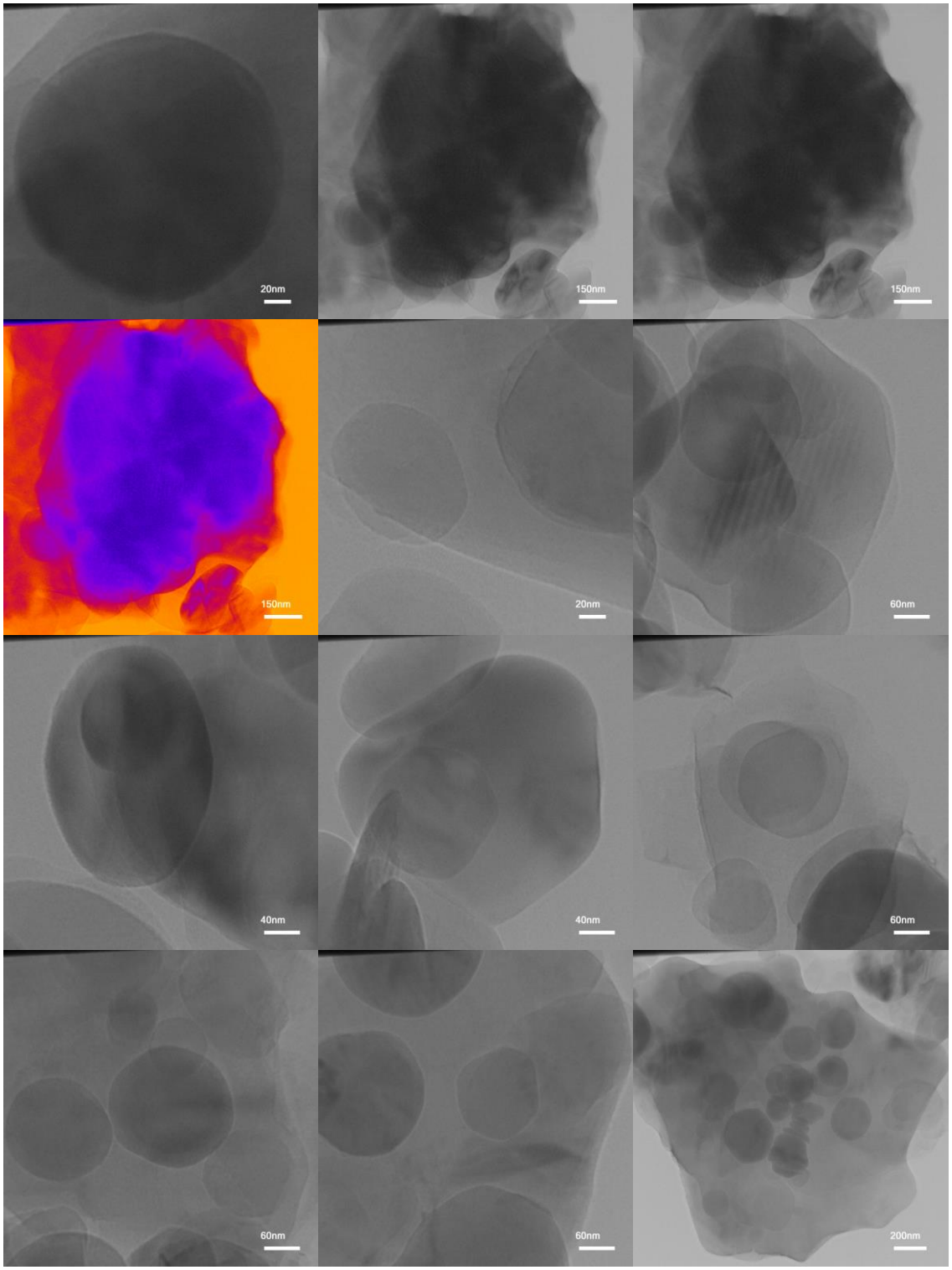


Figure S15. TEM images of Mn oxide/BN.

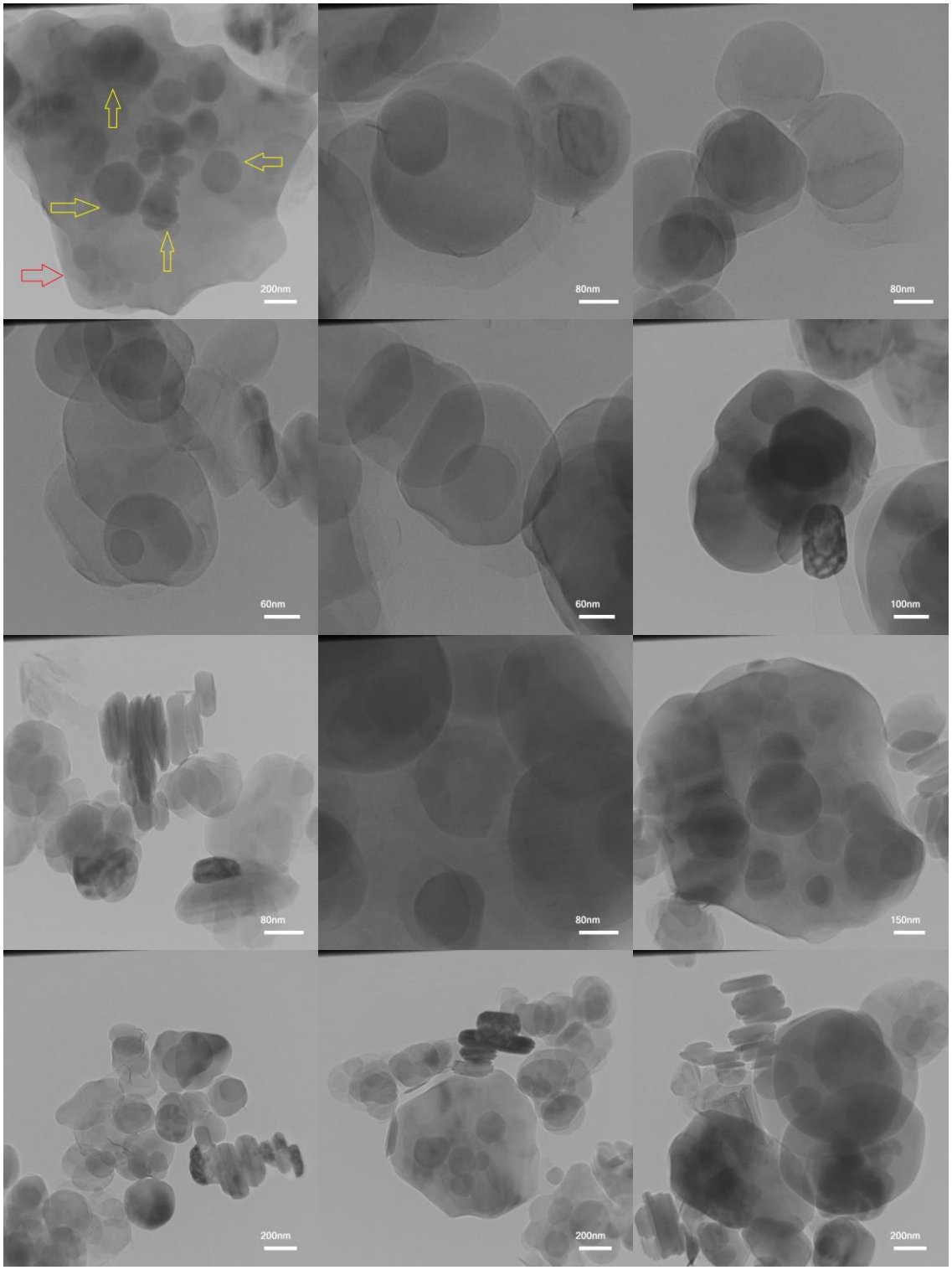


Figure S16. TEM images of Mn oxide/BN.

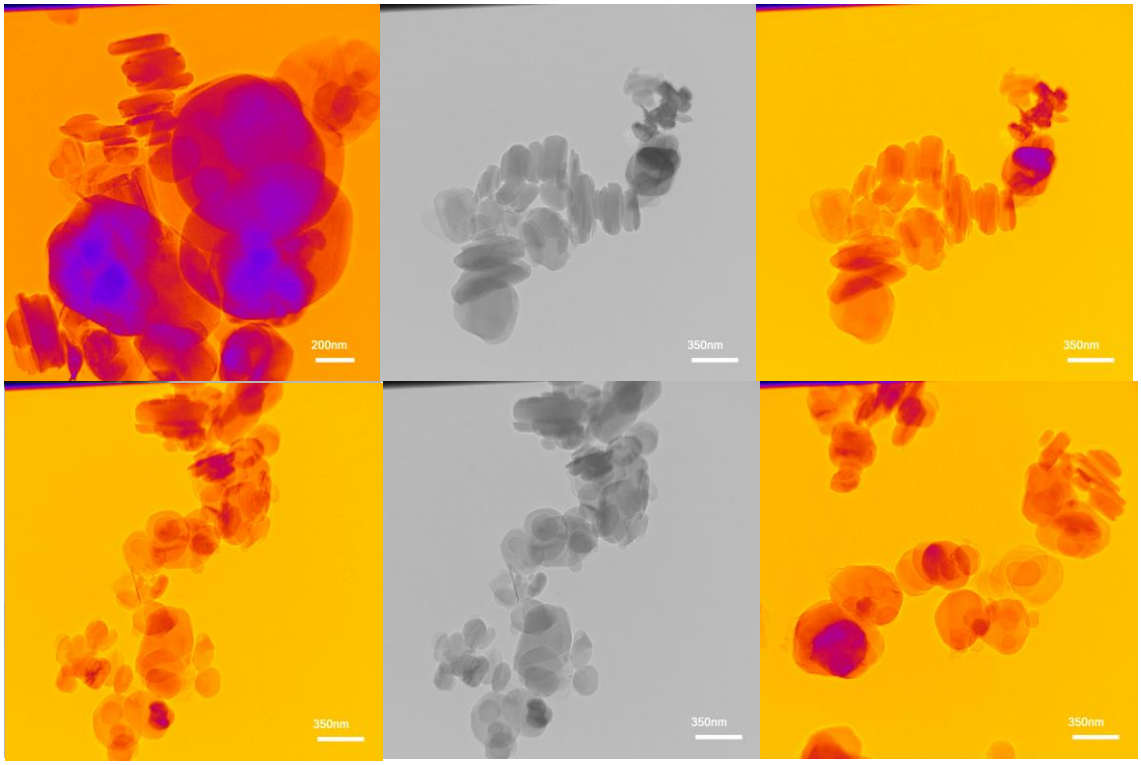


Figure S17. TEM images of Mn oxide/BN.

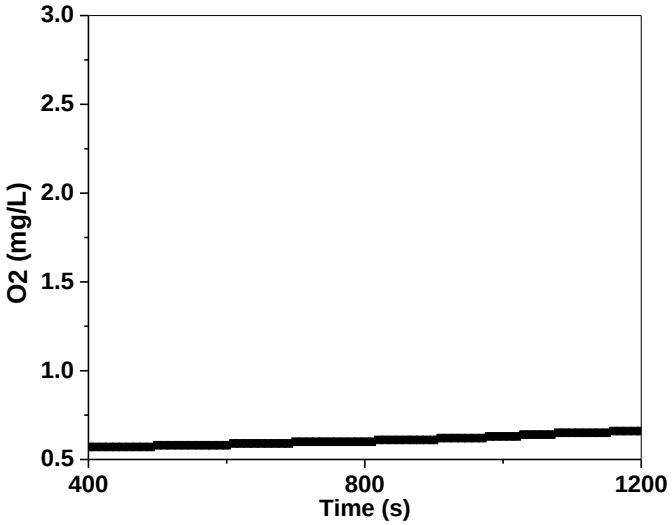
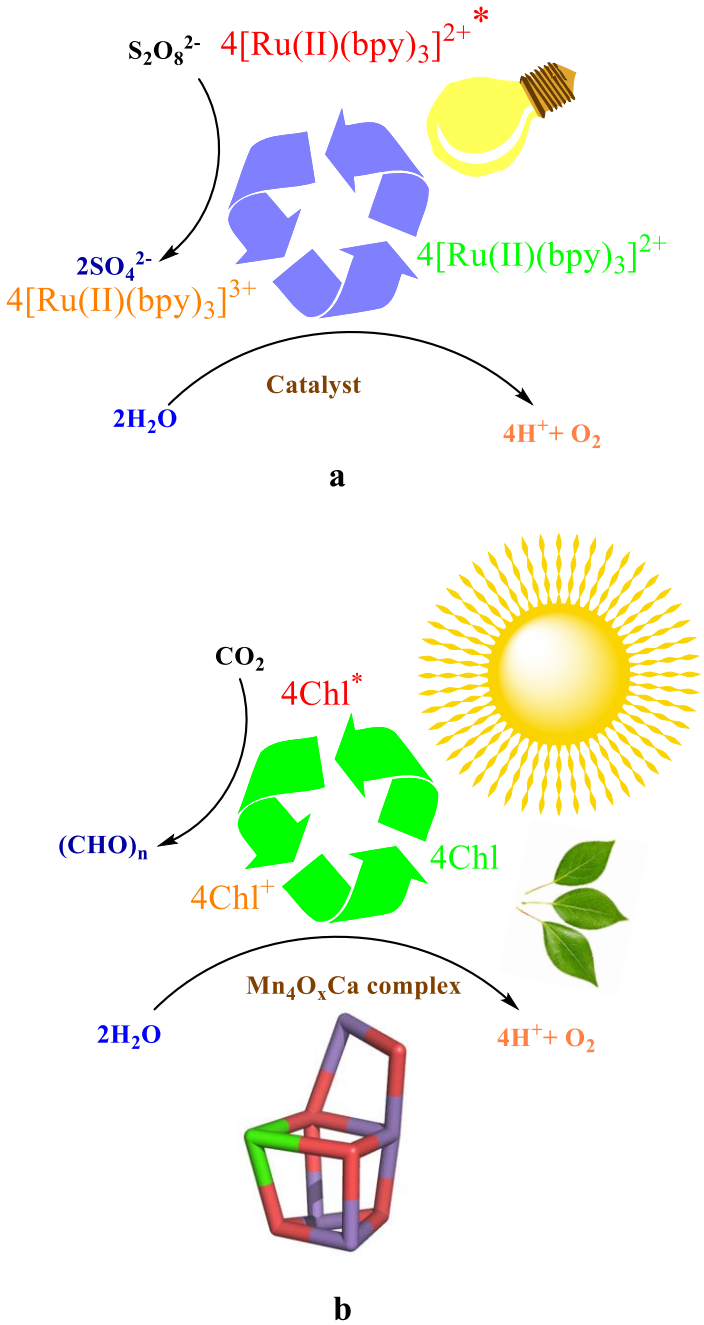


Figure S18 Oxygen evolution in the presence of pure BN (20.00 mg) ([Ce(IV)]: 0.11 M) at 25 ^{o}C.



Scheme S2 Comparison of the reactions involved in water oxidation in the presence of (a) $[Ru(II)(bpy)_3]^{3+}$ and (b) chlorophyll under light irradiation. The images was from ref. **R1** with modification.

Table S1 Rate of water oxidation by various Mn-based catalysts for water oxidation under the presence of non-oxo transfer oxidant. Data was from ref. 3. Table with modification is reprinted with permission from ref. **R2**. Copyright (2016) by American Chemical Society.

Compound	Oxidant	TOF $mmol_{O2}/s.mol_{Mn}$
calcined Mn oxide/BN at 200 °C	Ce(IV)	0.15
Nano scale Mn oxide within NaY zeolite	Ce(IV)	2.62
Layered Mn-Ca oxide	Ce(IV)	2.2
Layered Mn-Al, Zn, K, Cd and Mg oxide	Ce(IV)	0.8-2.2
Layered Ni(II) oxide	Ce(IV)	0.4-0.6
$CaMn_2O_4.H_2O$	Ce(IV)	0.54
Amorphous Mn Oxides	$Ru(bpy)_3^{3+}$ Ce(IV)	0.06 0.52
Nanosized Mn oxide on high surface (high surface) montmorillonite	Ce(IV)	0.5
Nanolayered Mn oxide	Ce(IV)	0.45
$CaMn_2O_4.4H_2O$	Ce(IV)	0.32
Mn oxide nanoclusters	$Ru(bpy)_3^{3+}$	0.28
β-MnO(OH)	CAN	0.24
Mn oxide-coated montmorillonite (low surface)	Ce(IV)	0.22
Layered Mn-Cu(II)	Ce(IV)	0.2-0.35
Mn_3O_4	CAN	0.01-0.17
Octahedral Molecular Sieves	$Ru(bpy)_3^{3+}$ Ce(IV)	0.11 0.05
MnO_2 (colloid)	Ce(IV)	0.09
α-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.059
$CaMn_3O_6$	Ce(IV)	0.046
$CaMn_4O_8$	Ce(IV)	0.035
α-MnO_2 nanotubes	$Ru(bpy)_3^{3+}$	0.035
Mn_2O_3	Ce(IV)	0.027
β-MnO_2 nanowires	$Ru(bpy)_3^{3+}$	0.02
$Ca_2Mn_3O_8$	Ce(IV)	0.016
$CaMnO_3$	Ce(IV)	0.012
Nanosized λ-MnO_2	$Ru(bpy)_3^{3+}$	0.03
Bulk α-MnO_2	$Ru(bpy)_3^{3+}$	0.01
Mn Complexes	Ce(IV)	0.01-0.6
Photosystem II	Sunlight	$100\text{-}400 \times 10^3$

References

R1 M. M. Najafpour, T. Ehrenberg, M. Wiechen, P. Kurz, *Angew. Chem. Int. Ed.*, 2010, 49, 2233.

R2 M. M. Najafpour, G. Renger, M. Hołyńska, A. Nemati Moghaddam, E. M. Aro, R. H. Carpentier, H. Nishihara, J. J. Eaton-Rye, J. R. Shen and S. I. Allakhverdiev, *Chem Rev*., 2016, **116**, 2886.