Electronic Supplementary Information

Carbon for engineering of a water-oxidizing catalyst

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Contents

Characterizations from TurboBeads™ Amine, which was purchased from Sigma-Aldrich:

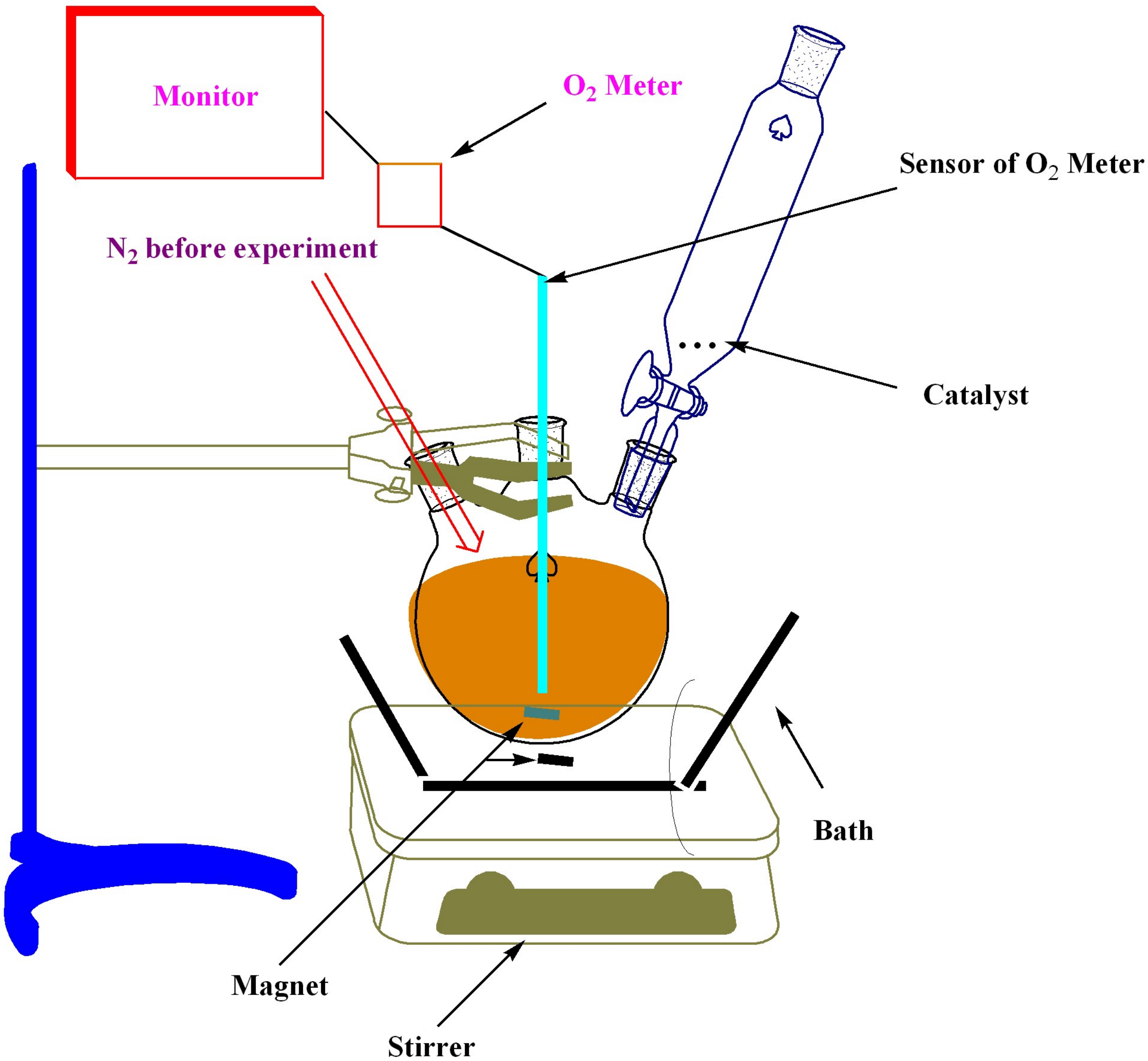
Assay	≥ 99%
Composition	carbon content, ≤ 14 wt. %
Nitrogen content	nitrogen content, ≥ 0.14%
Extent of labeling	≥ 0.1 mmol/g loading (-Ph-CH_2-NH_2)
Magnetization	≥ 120 emu/g, mass saturation
Aaverage diameter	≤ 50 nm
Surface area	spec. surface area ≥ 15 m^2/g
Suitability	conforms to structure for Infrared spectrum

Water Oxidation

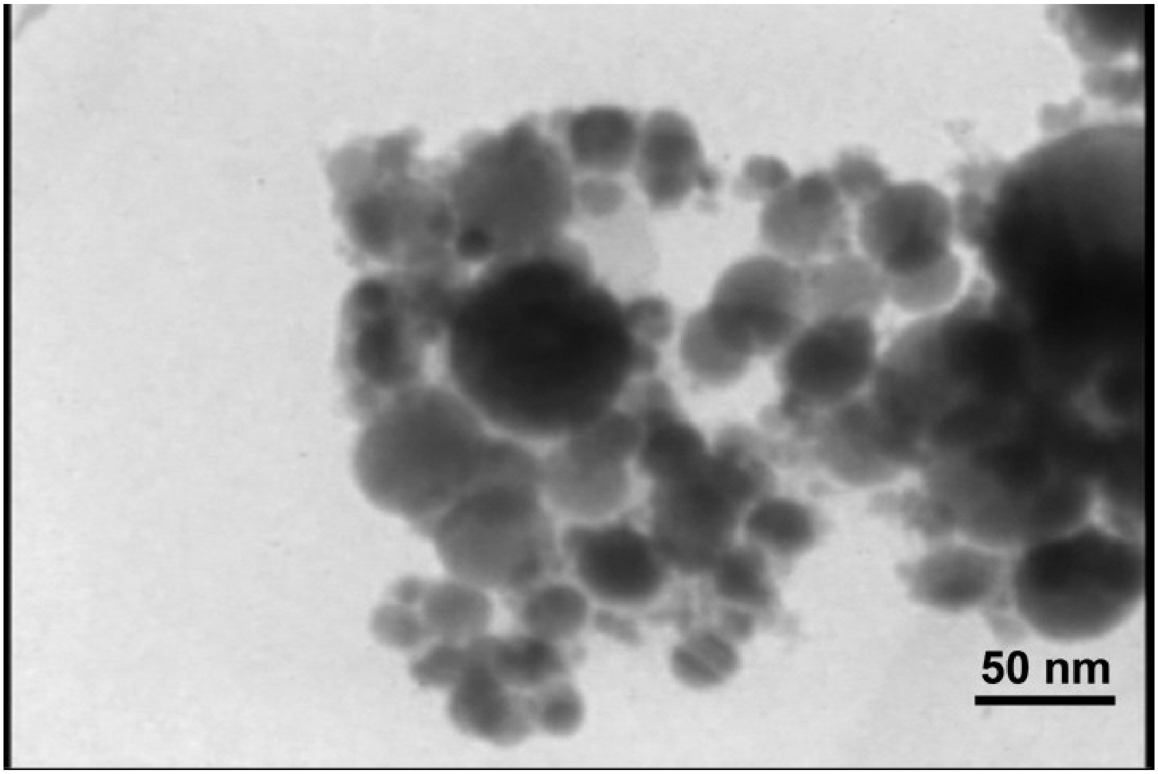
Oxygen evolution from aqueous solutions in the presence of Ce(IV) was investigated using an HQ40d portable dissolved oxygen-meter connected to an oxygen monitor with digital readout. The reactor was maintained at 25.0 ºC in a water bath. In a typical run, the instrument readout was calibrated against 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 under these conditions and oxygen evolution was not observed. After deaeration of the Ce(IV) solution with argon, **MnT** as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring. 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 was performed by a set up shown in Scheme S1.

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

Photochemical water oxidation experiments were performed in a flask containing 10 mL of aqueous buffer (Na_2SiF_6-$NaHCO_3$, 0.022-0.028 M) with pH held at 5.8, Na_2SO_4 (150 mg), $K_2S_2O_8$ (800 mg), $[Ru(bpy)_3]Cl_2·6H_2O$ (15 mg), and **1 (**20 mg). After deaeration of the solution by Ar, the reactor was irradiated with 4 LED (each one 10 W, 500 nm) around flask in a home-made device.



Scheme S1 Set up for water-oxidation experiments.



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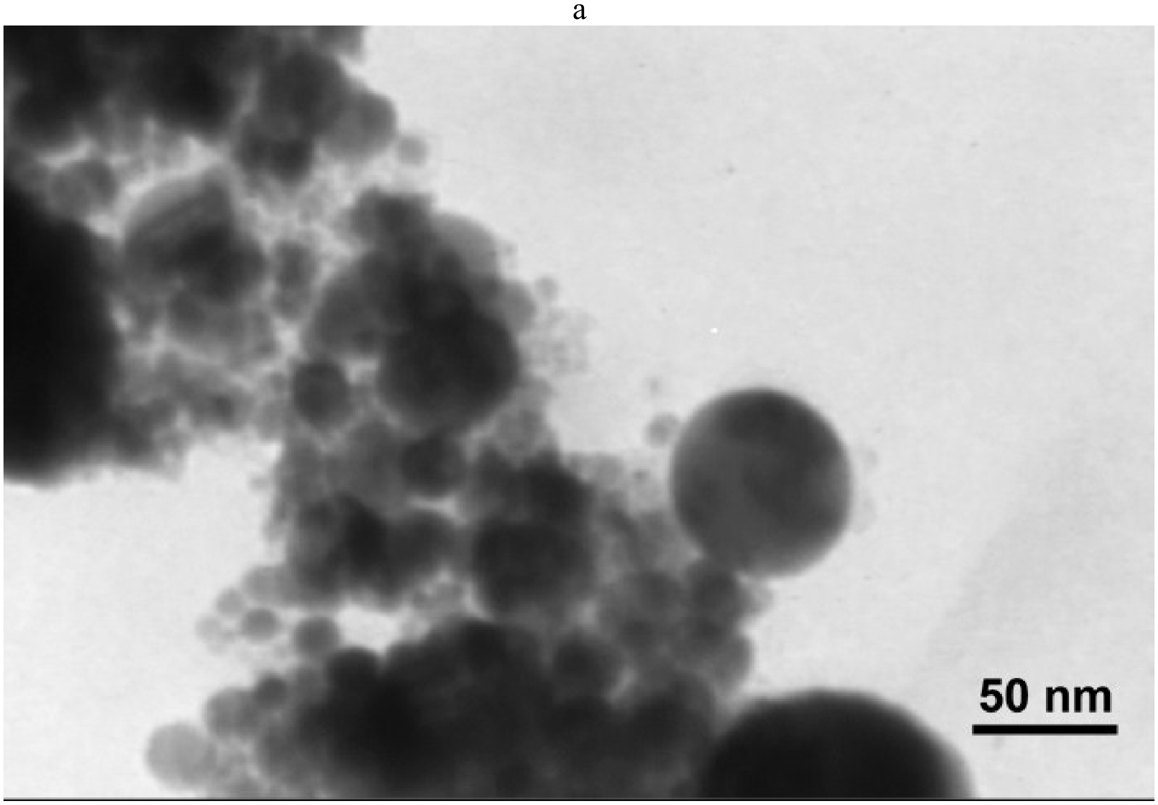

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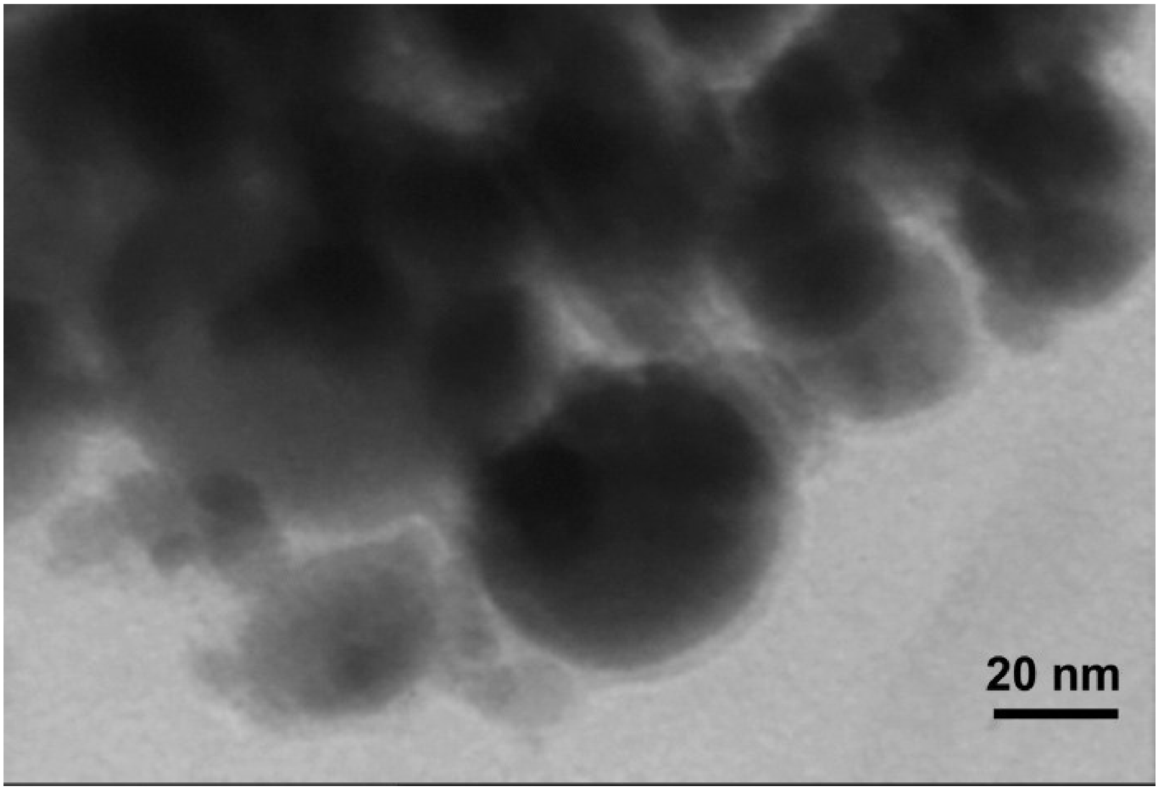

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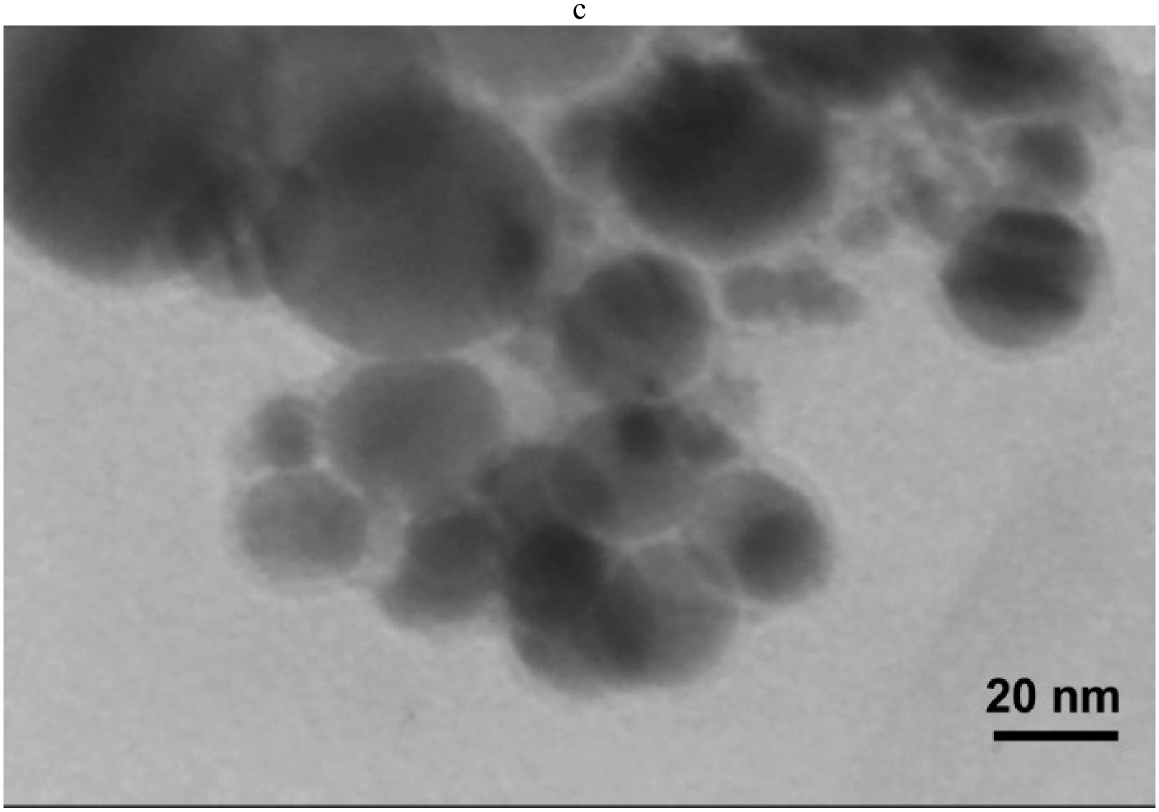

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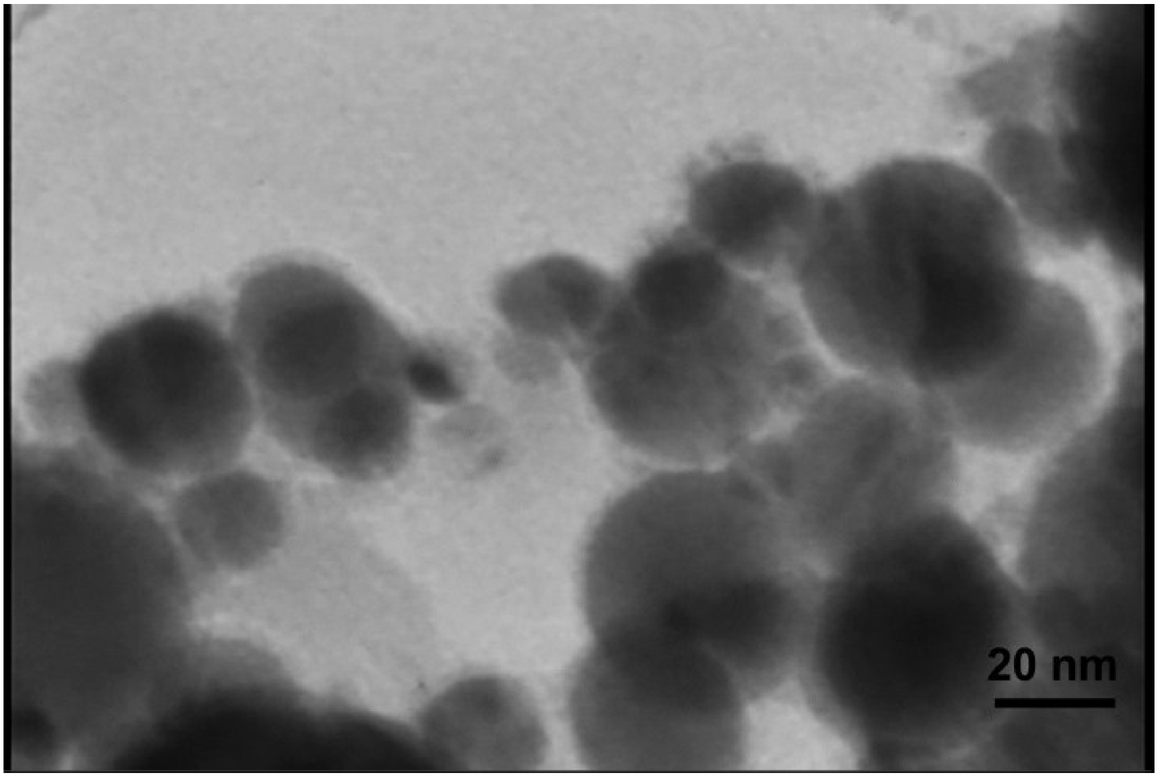

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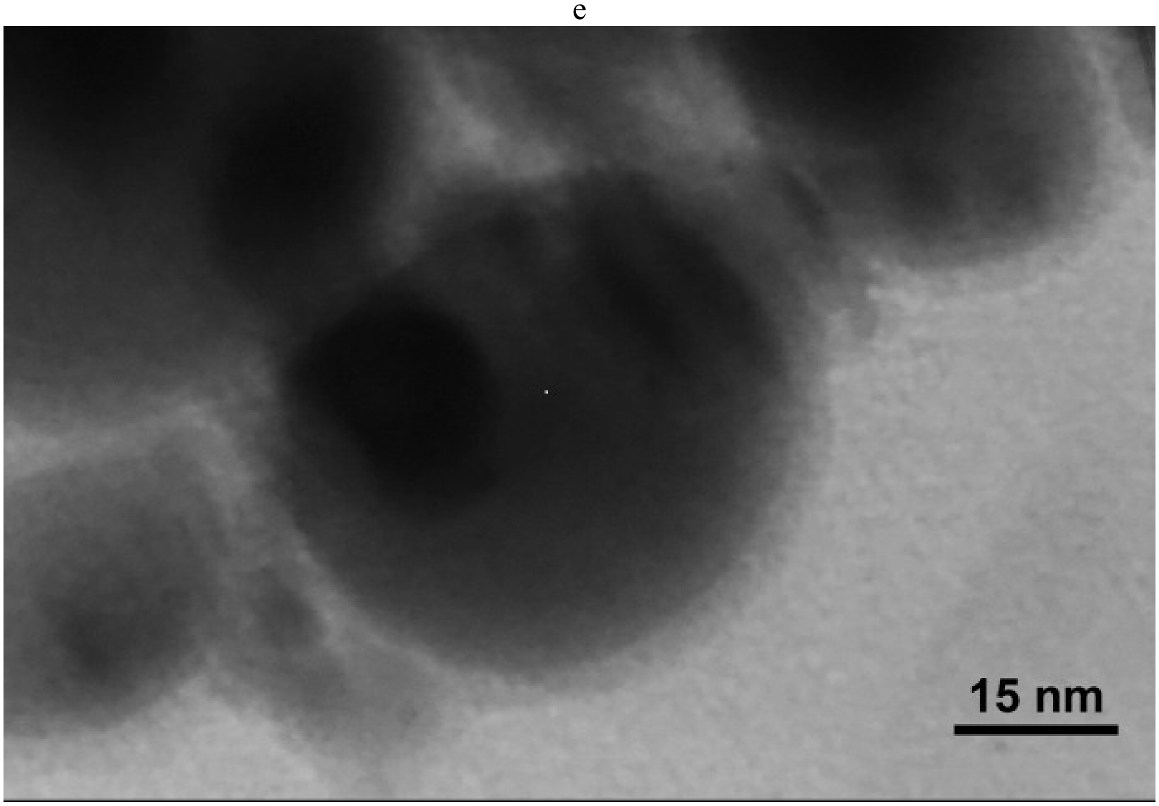

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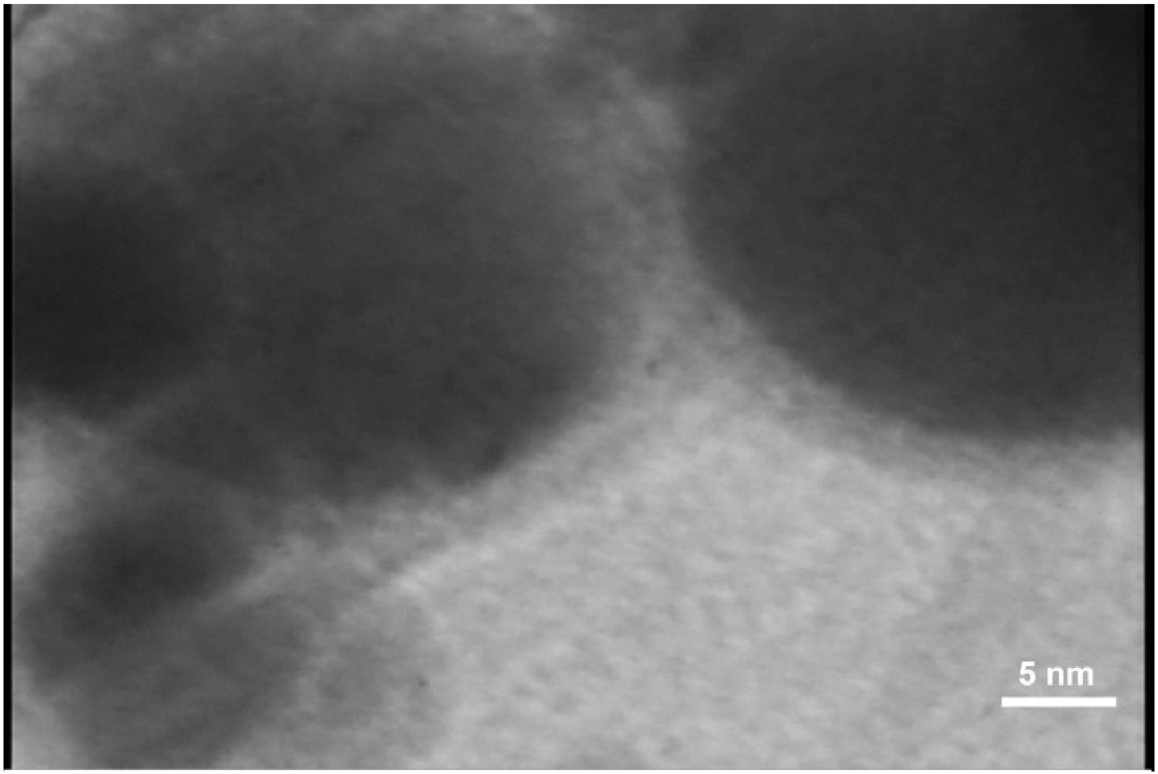
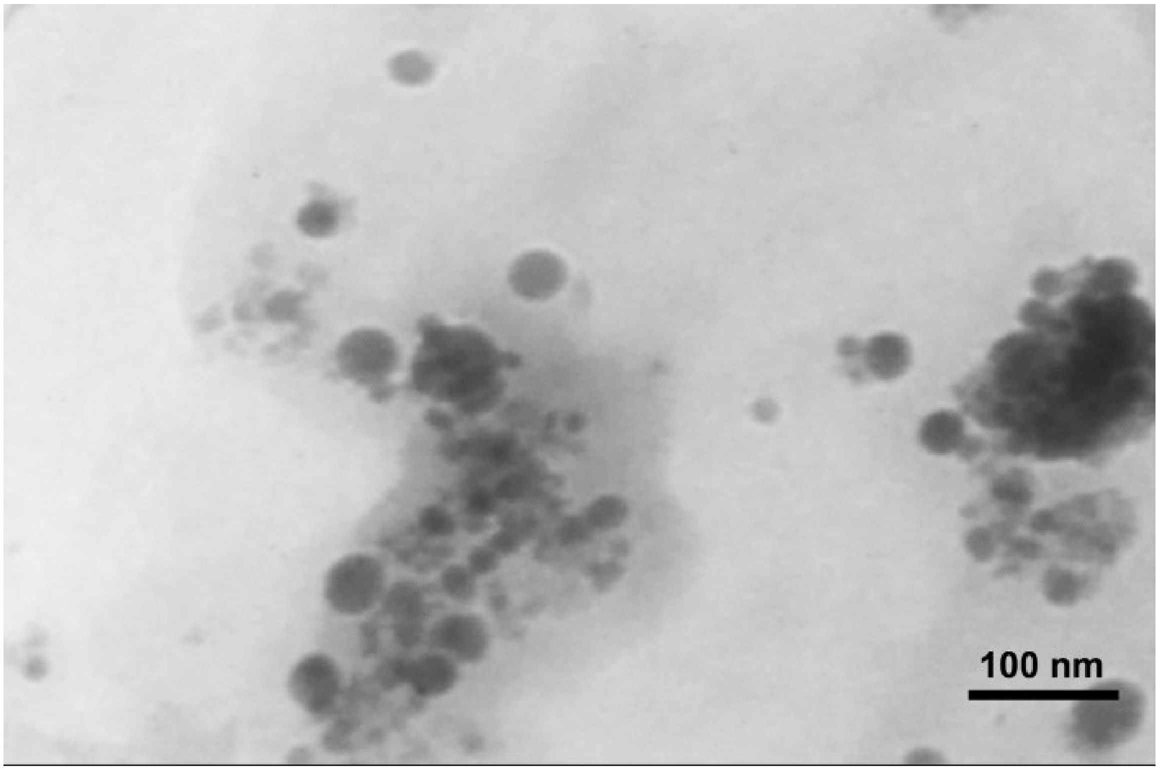
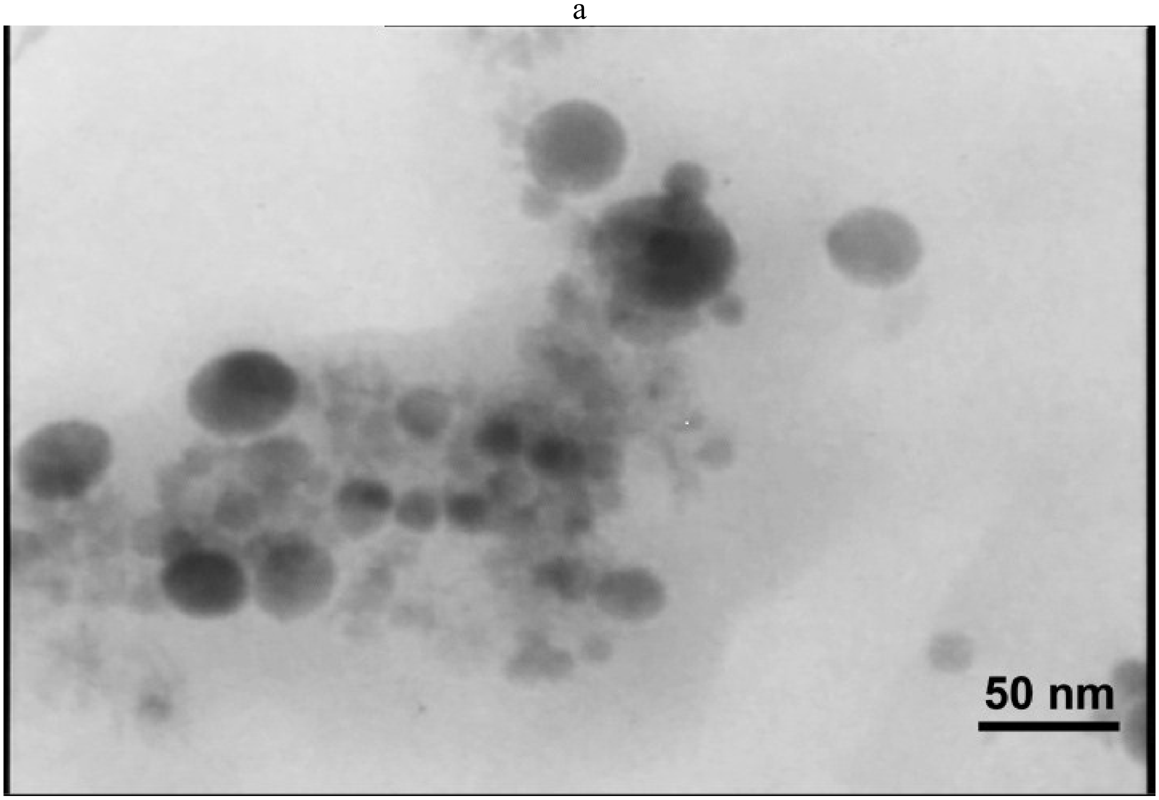


g

Fig. S1 TEM images of **T** (a-g).



a



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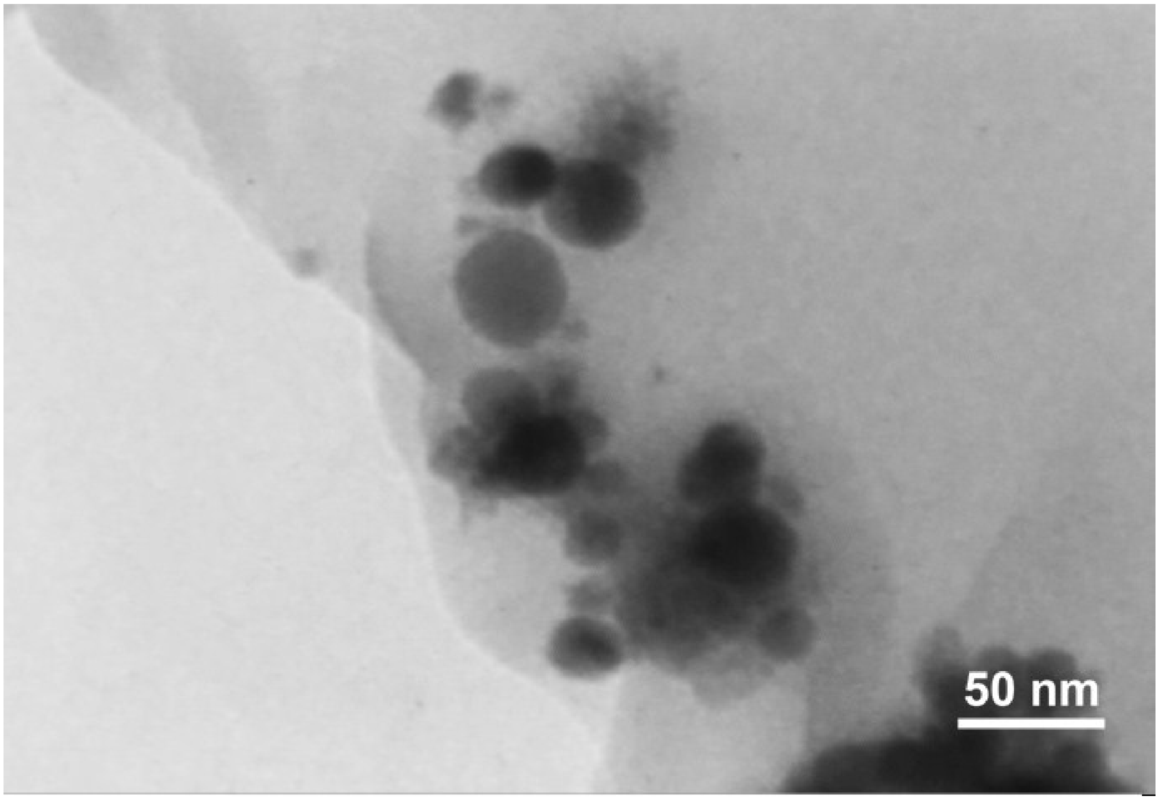
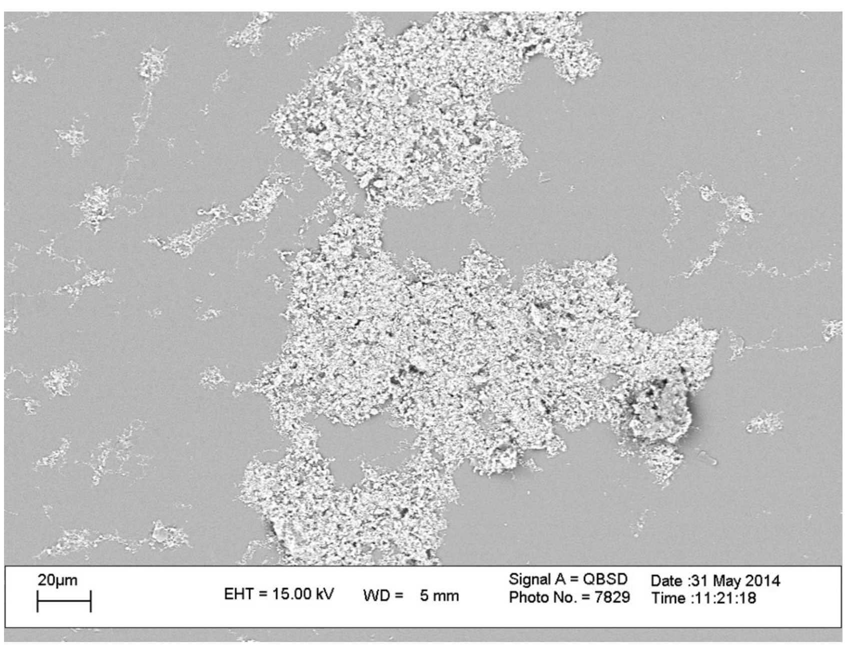


c

Fig. S2 TEM image of **MnT**.



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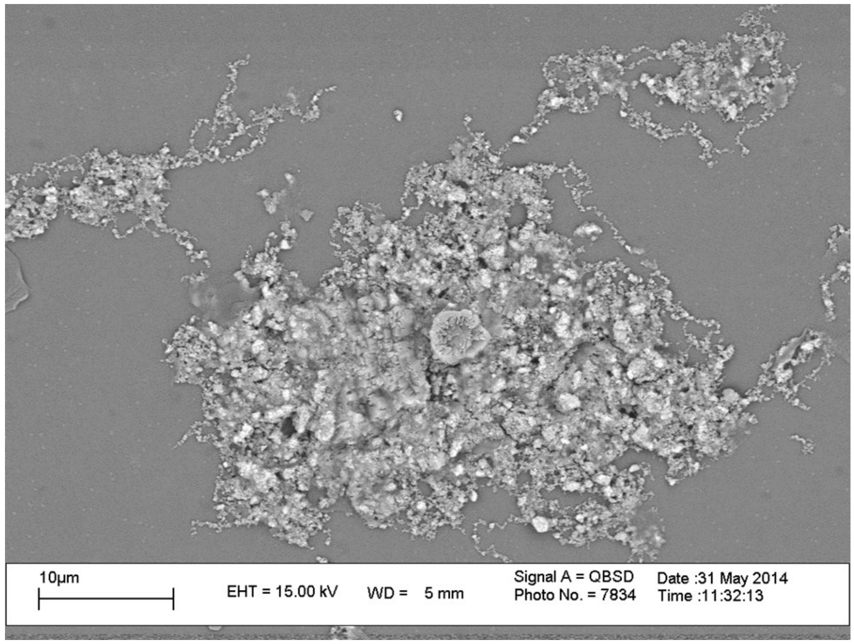
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WD = 5 mm
Signal A = QBSD
Photo No. = 7834
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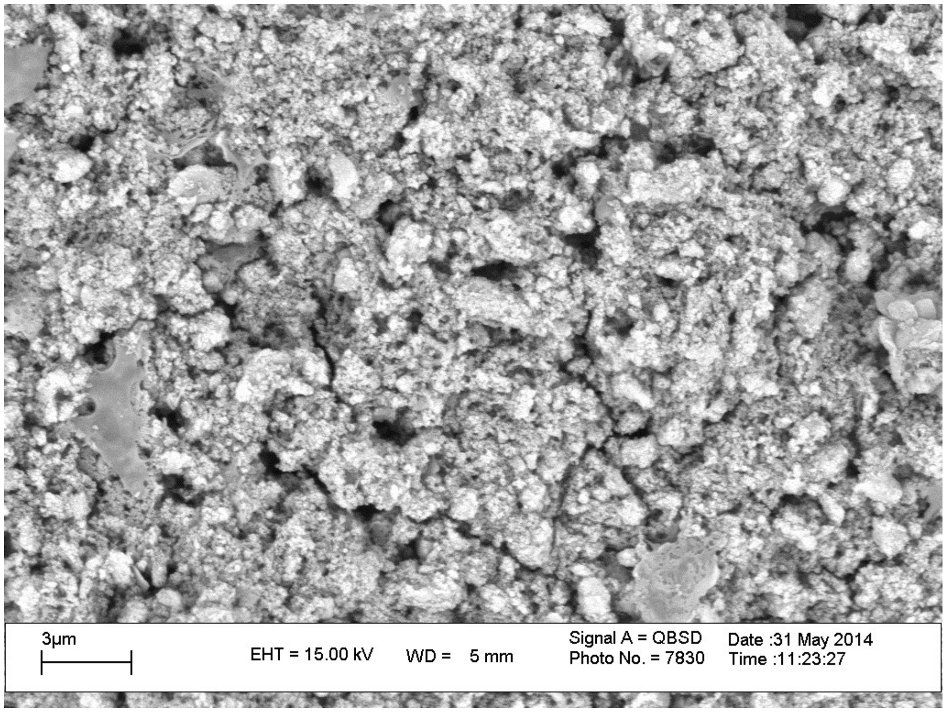
Time :11:32:13

b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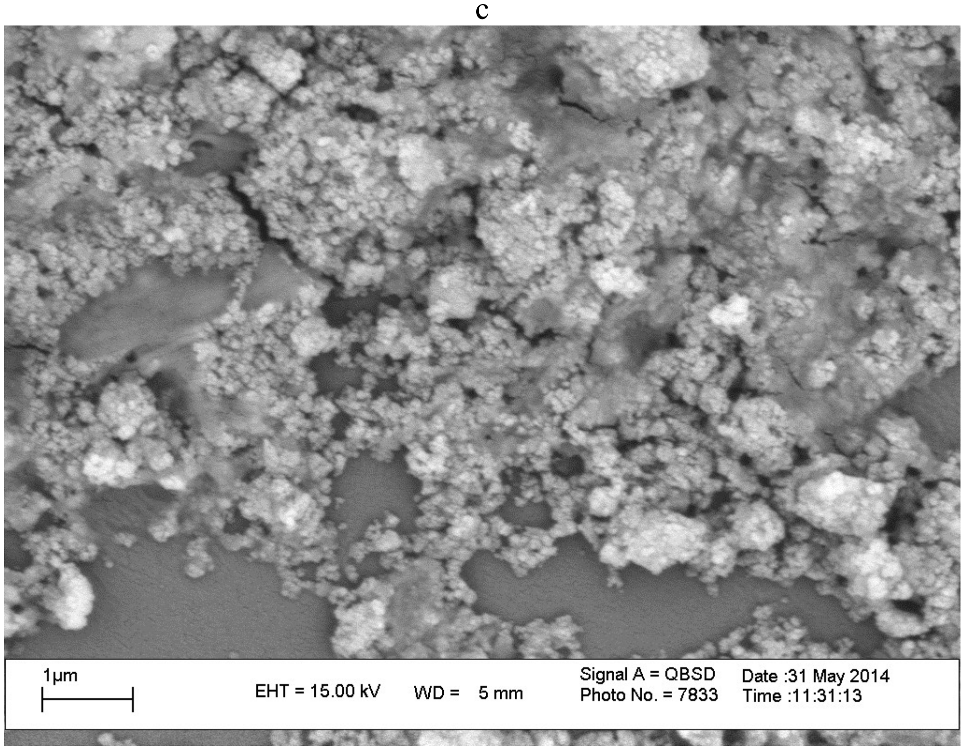
c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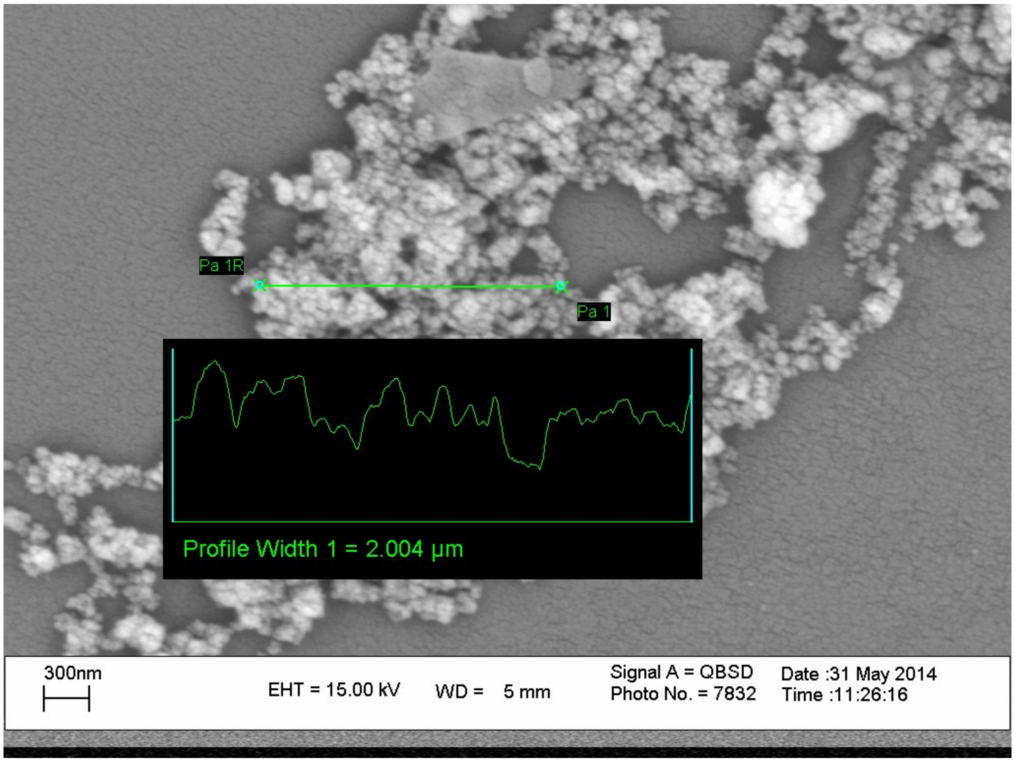
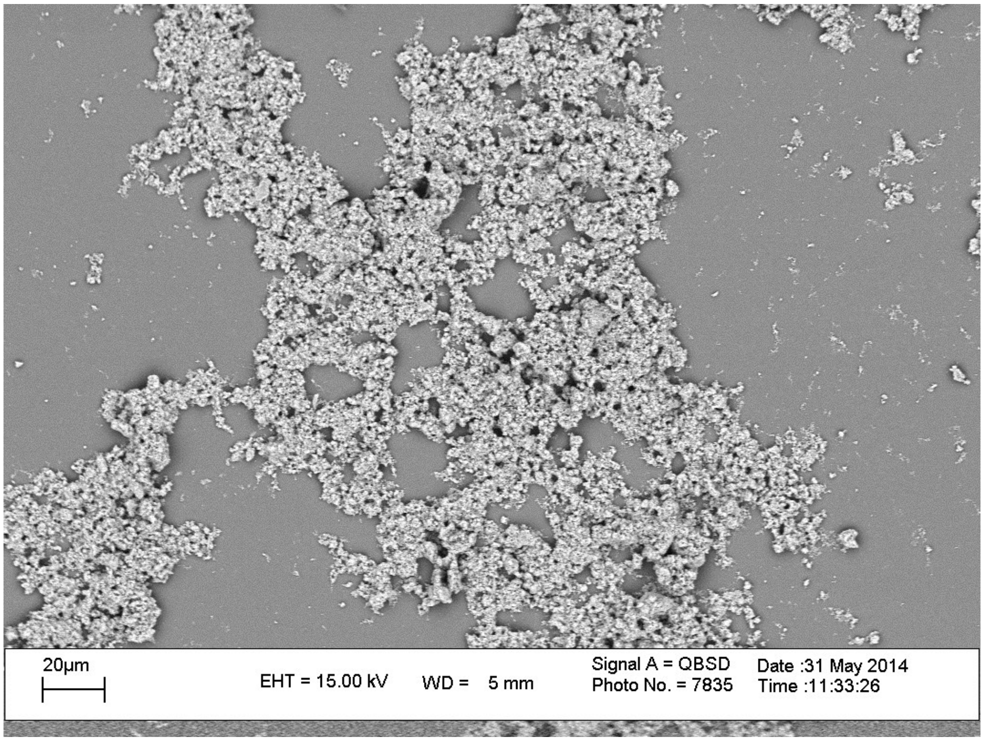
d

e



f

Fig. S3 SEM images of **T**.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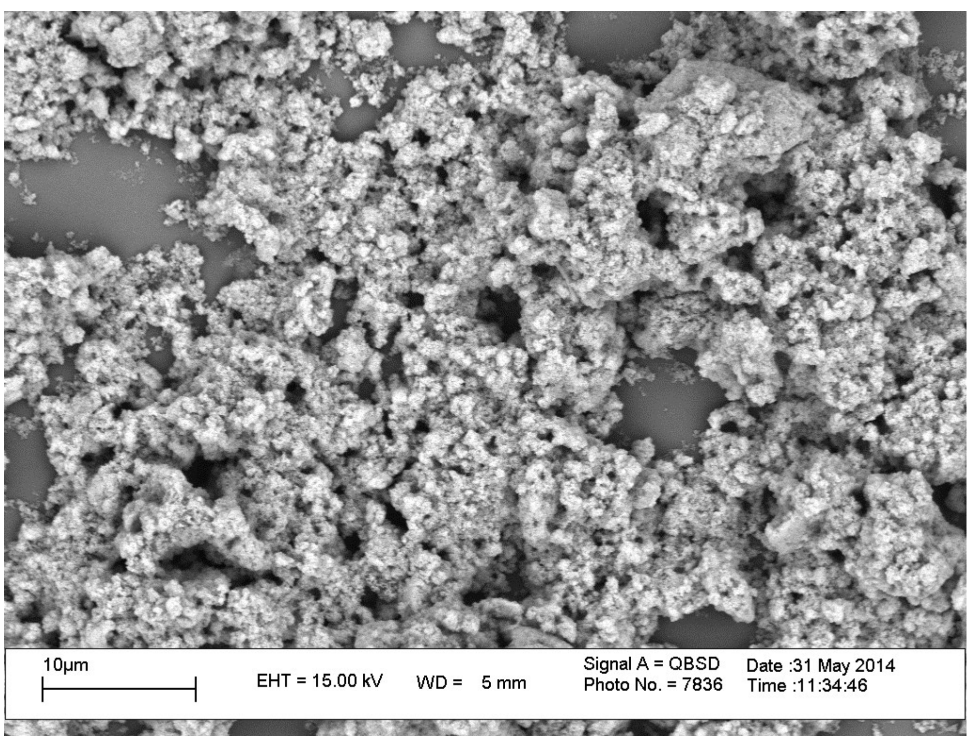
Time :11:33:26

a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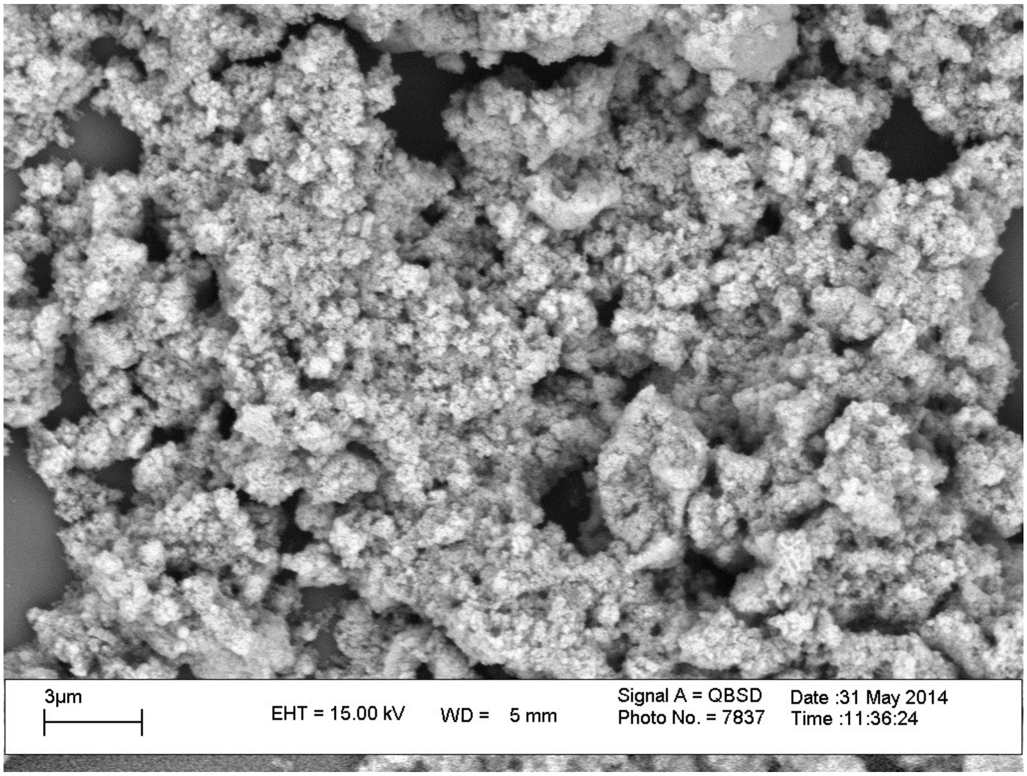
b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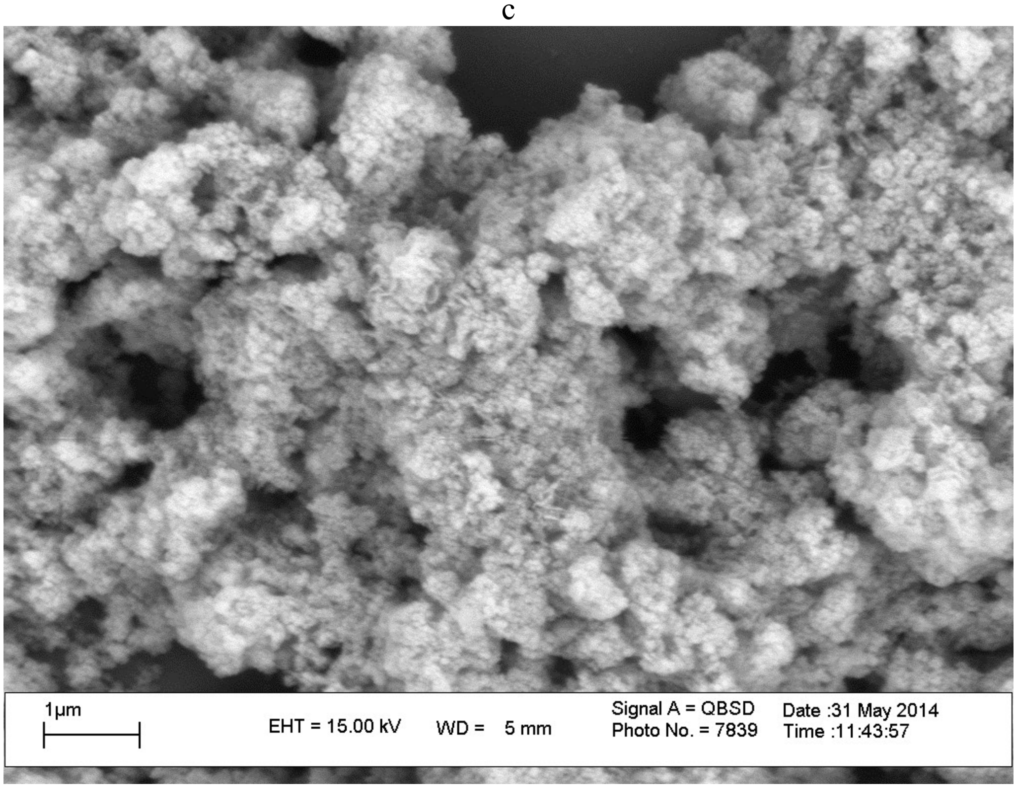
c


1µm
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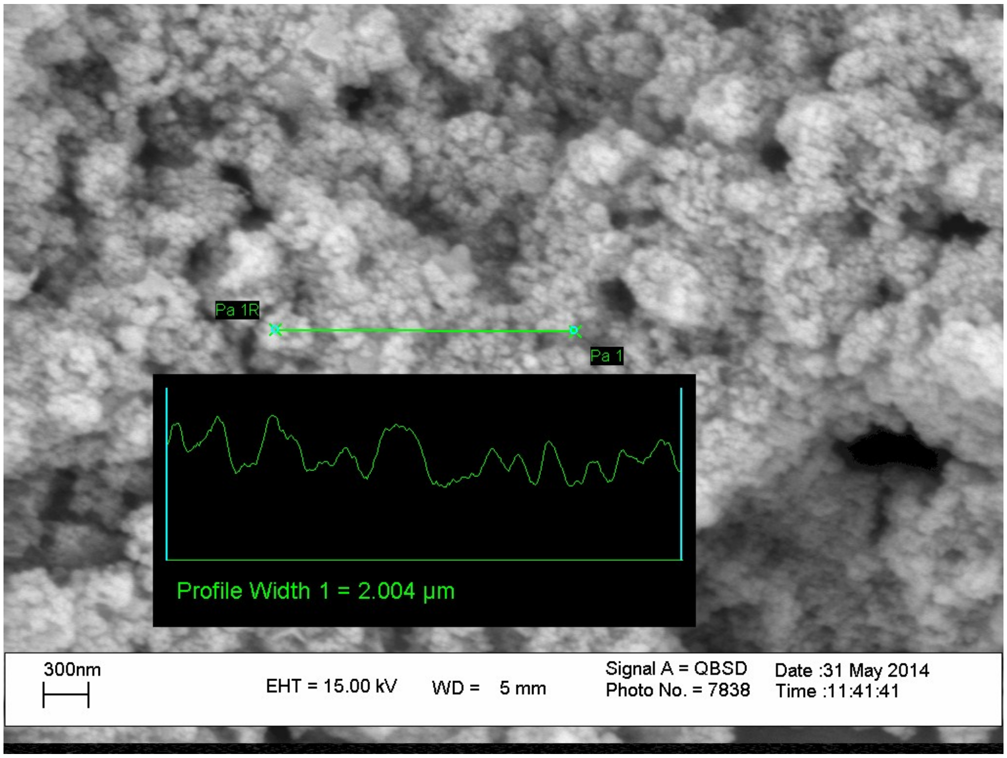
d



e

Fig. S4 SEM images of **MnT**.