Electronic Supplementary Material (ESI) for Dalton Transactions

Supplementary Information

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2-(2-Hydroxyphenyl)-1H-benzimidazole-manganese oxide hybrid as a promising structural model for Tyrosine 161/Histidine 190-manganese cluster in Photosystem II

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Methods

All the reagents and the solvents were purchased from commercial sources and were used without further purification. Mid Infrared spectra of KBr pellets of compounds were recorded on a Bruker vector 22 between 400 and 4000 cm^{-1}. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorbtion Spectrometer Varian Spectr AA 110. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. Cyclic voltammetry and amperometric studies were performed, using an Autolab potentiostat-galvanostat model PGSTAT30 (Utrecht, The Netherlands) with a conventional three electrode set-up, in which a Pt or Pt modified electrode with the model compound **1** or the dried manganese (III, IV) oxide monosheets, an $Ag|AgCl|KCl_{sat}$ and a platinum rod served as the working, reference and auxiliary electrode, respectively. The working potential was applied in the standard way using the potentiostat and the output signal was acquired by Autolab Nova software.

Preparation of Colloidal Birnessite Monosheets:[1]

20.0 mL of a mixed aqueous solution of tetramethylammonium (TMA) hydroxide (0.6 M) and 3.0 % (by wt) of H_2O_2 was added to 10 mL of 0.3 M $MnCl_2 \cdot 4H_2O$ aqueous solution. The resulting dark brown suspension was stirred vigorously overnight in the open air at room temperature. Dried aggregate was separated by filtration (Millipore, type-JH, 0.45 μm pore size), washed with copious amounts of distilled water, and then air-dried at room temperature.

Preparation of model compound 1:

2-(2-Hydroxyphenyl)-1H-benzimidazole (210.2 mg, 1.00 mmol) was dissolved in 10 mL water (at pH ~ 6, using glacial acetic acid) and the solution was added to 50 mL of the colloidal suspension of MnO_2 monosheets (4 mM) during argon bubbling at room temperature. Immediately after this addition, flocculation occurred in the mixed solution. The resulting brown precipitate was filtered off, washed with water, air-dried at room temperature and then dried under vacuum.

Preparation of modified electrode

A bare glassy carbon electrode was polished with 1, 0.3 or 0.05 μm alumina slurry, and then thoroughly rinsed by ethanol and distilled water, and washed ultrasonically to get a mirror-like finish. The cleaned Pt electrode was dried with nitrogen steam for further modification. The prepared dried manganese (III, IV) oxide monosheets or suspension of compound **1** was dispersed, ultrasonically, in water. The modified electrode was prepared by dropping 20 μL of **1** suspension ($0.1 mg.mL^{-1}$) on the Pt electrode surface and dried at room temperature. The electrochemical properties of different electrodes were investigated by cyclic voltammetry (CV) in a 0.1M pH 6.3 lithium perchlorate solution.

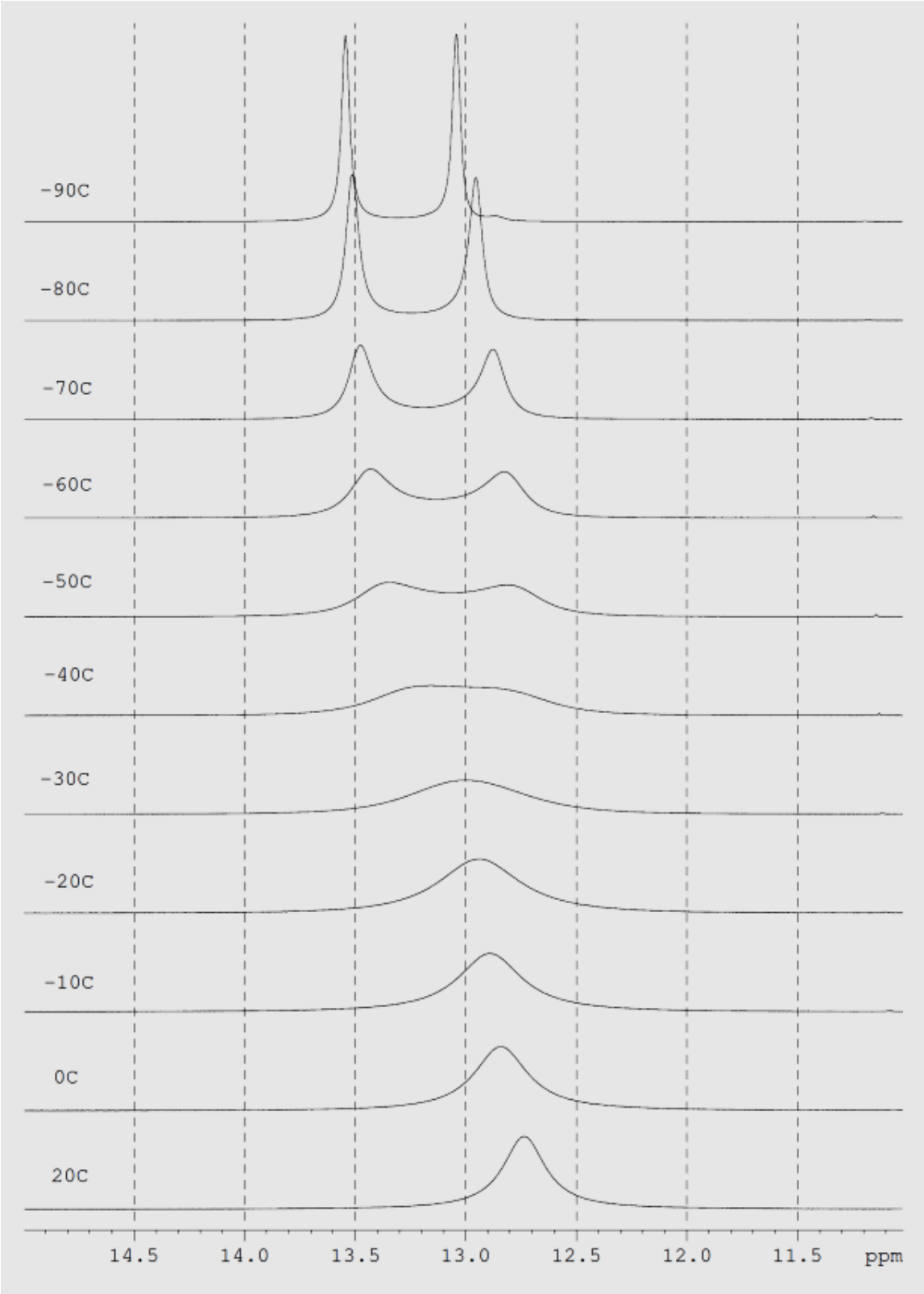
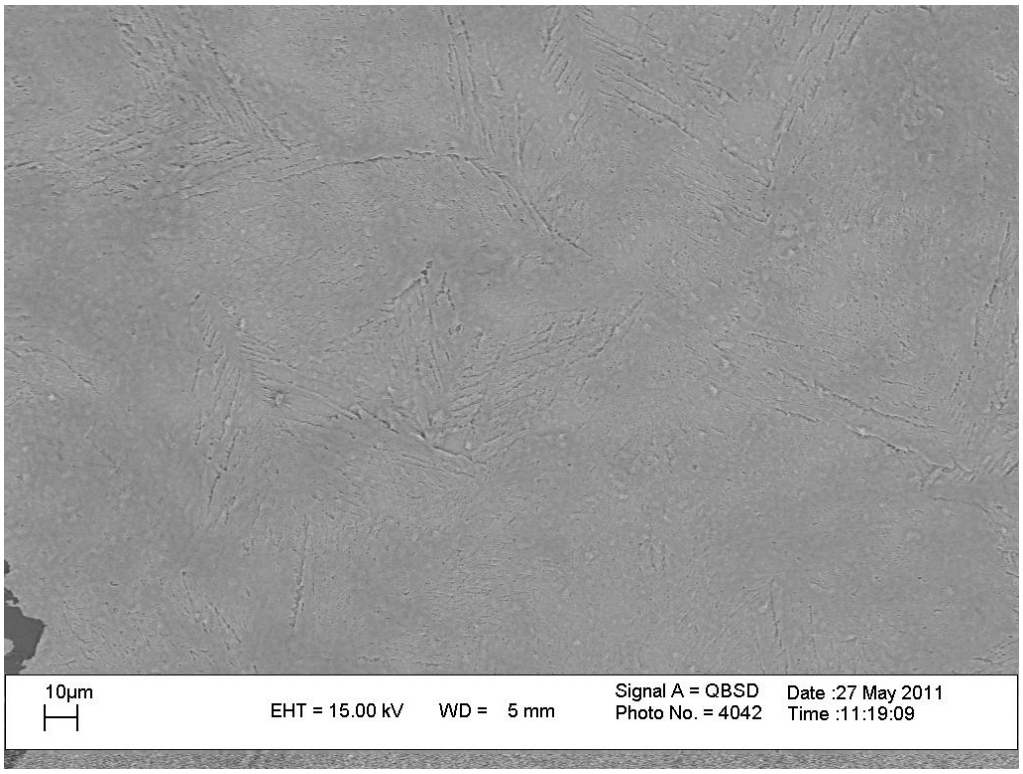


Fig. S1The ^{1}HNMR spectra of IP in acetone-d_6 clearly show a downfield shift of the O-H resonance to >13 ppm that is characteristic of an intramolecular H-bond.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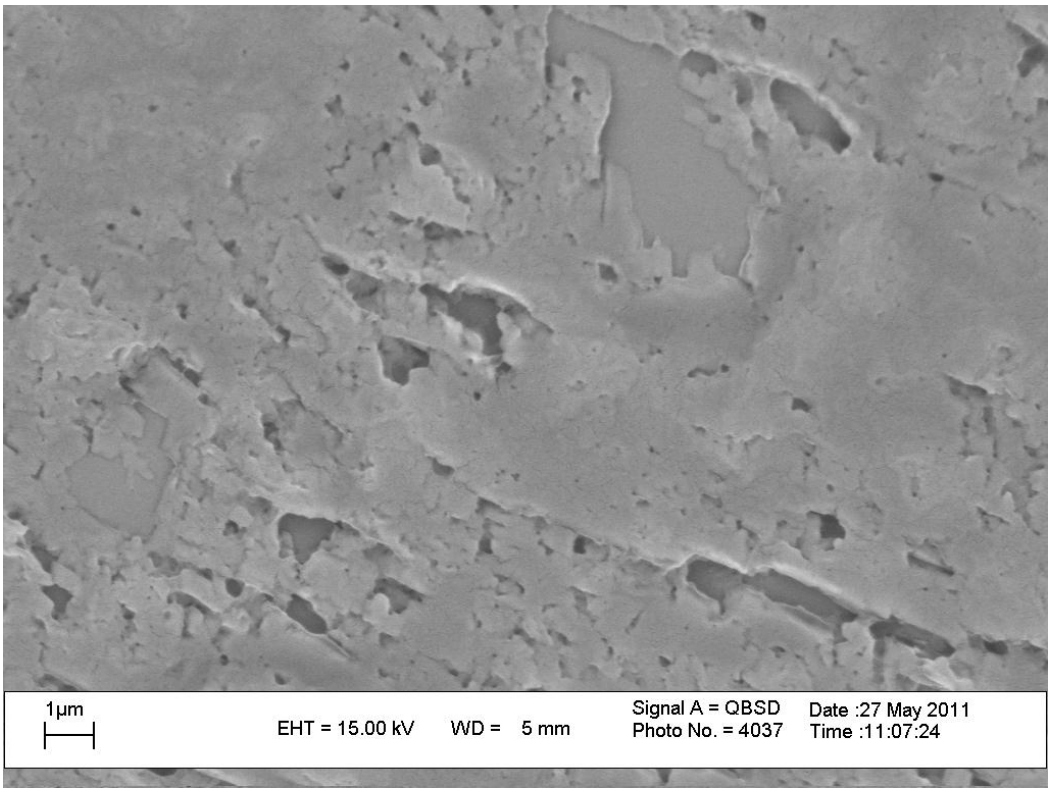
a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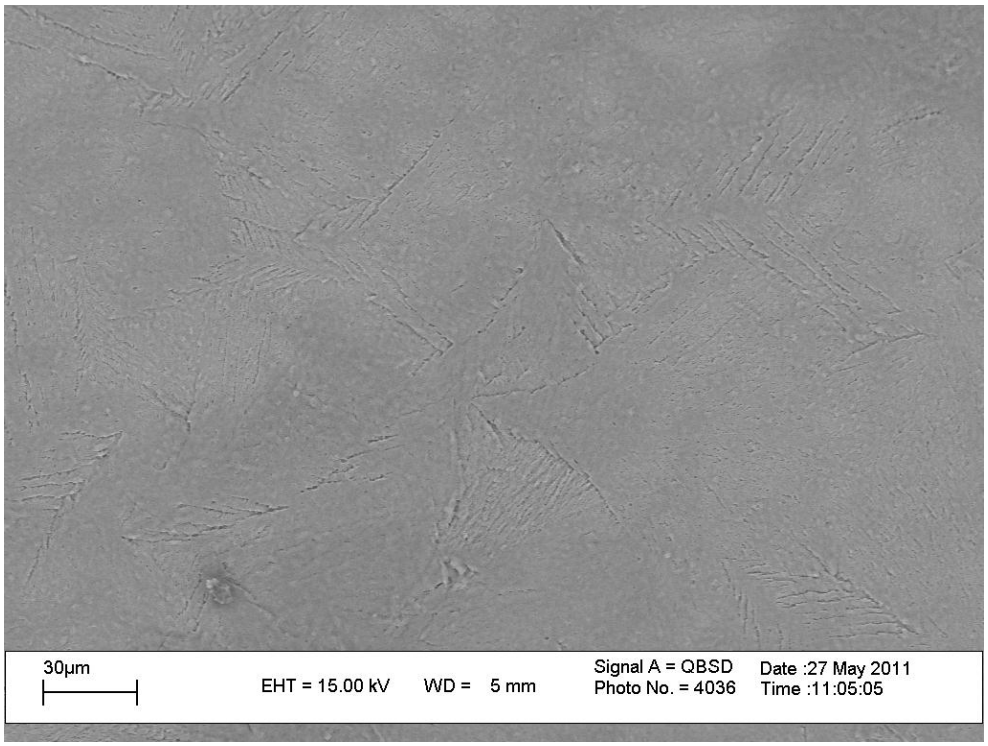
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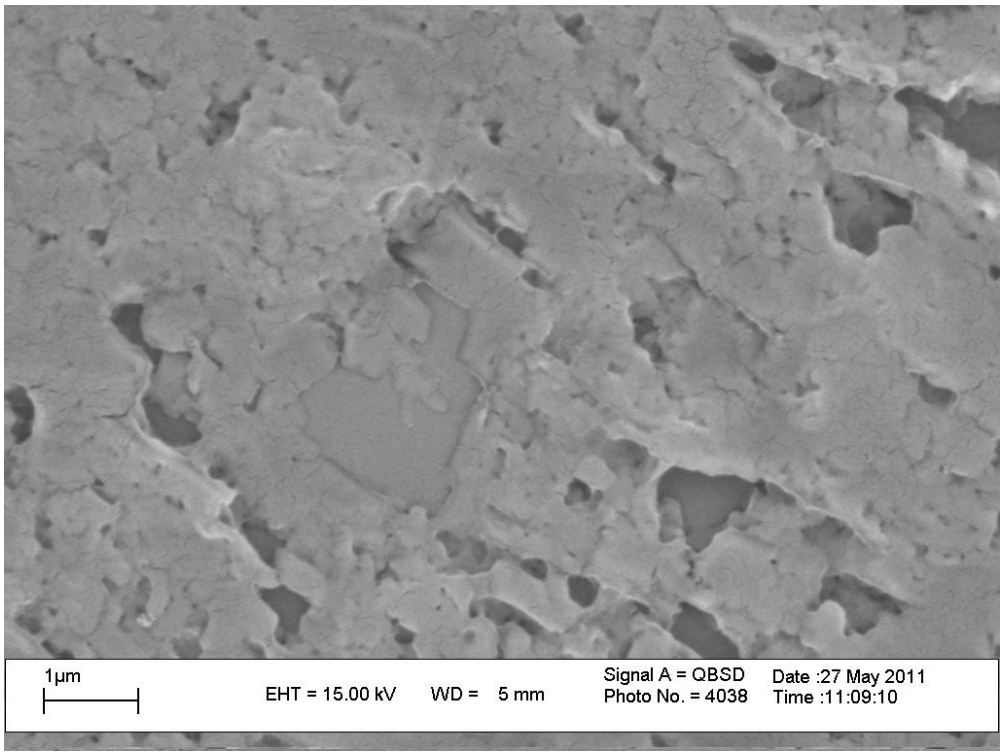
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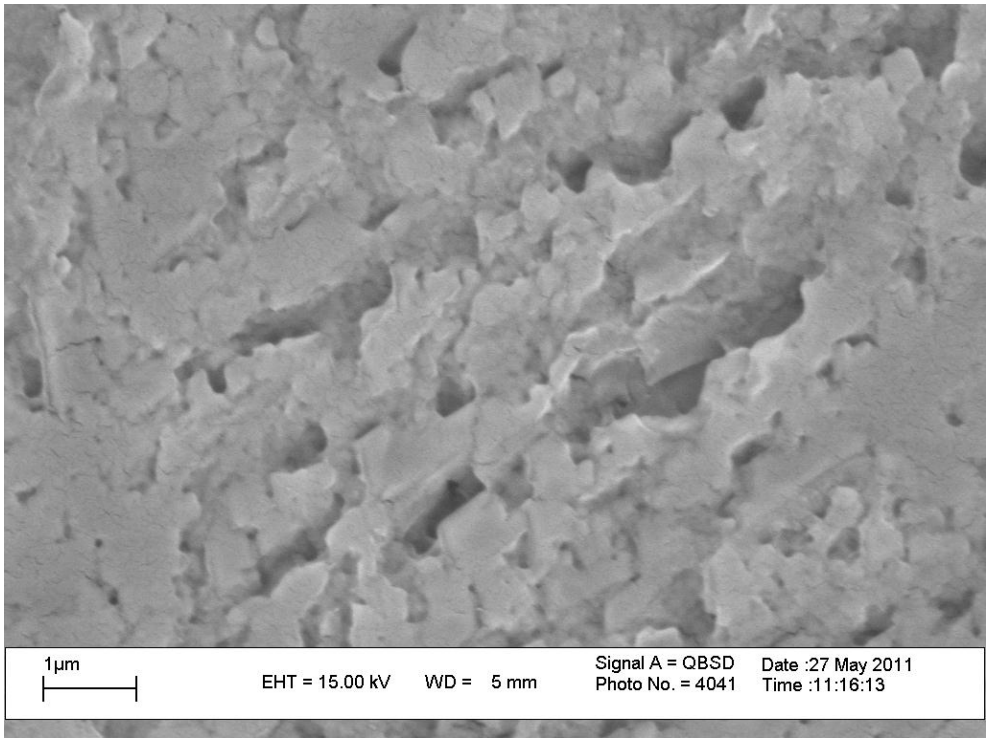
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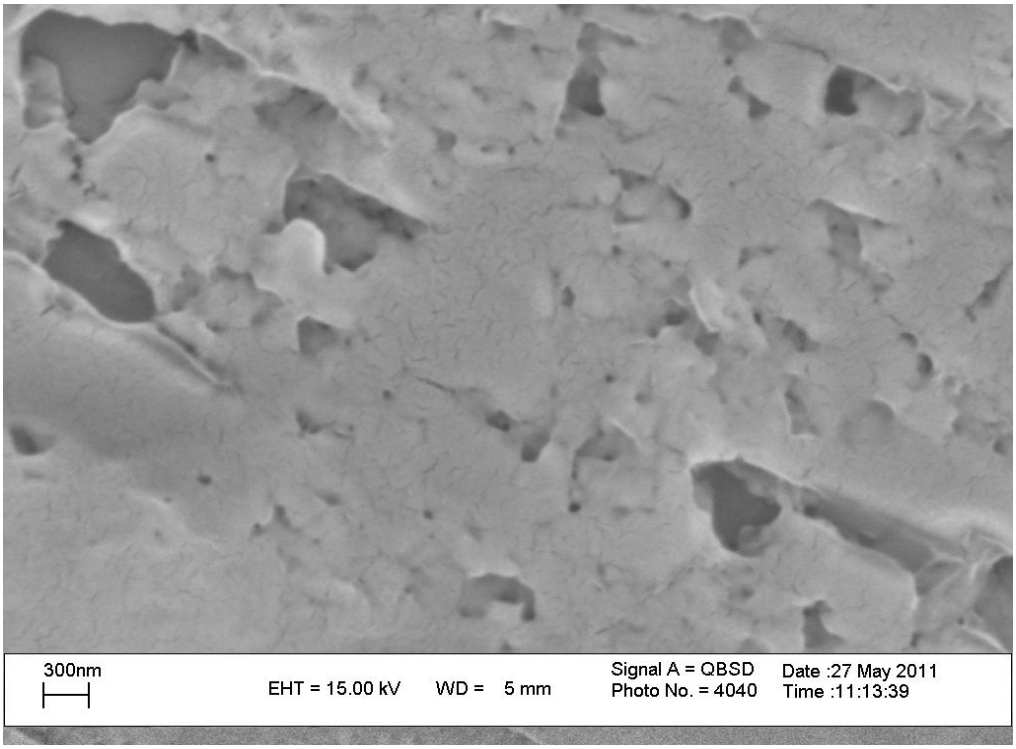
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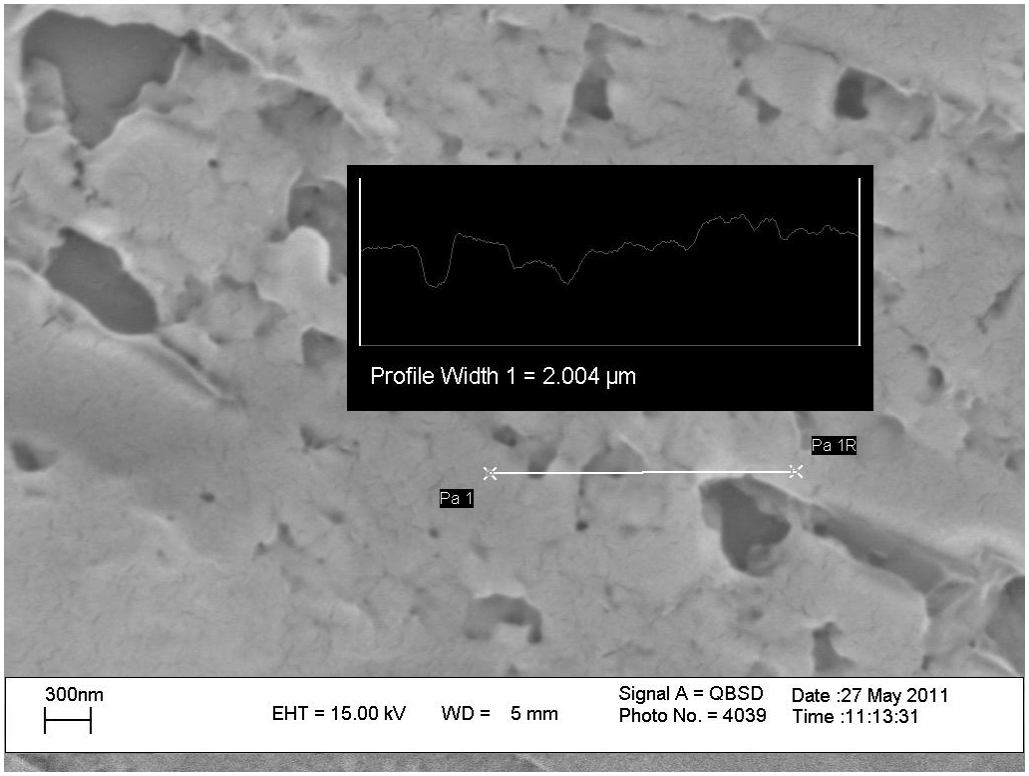
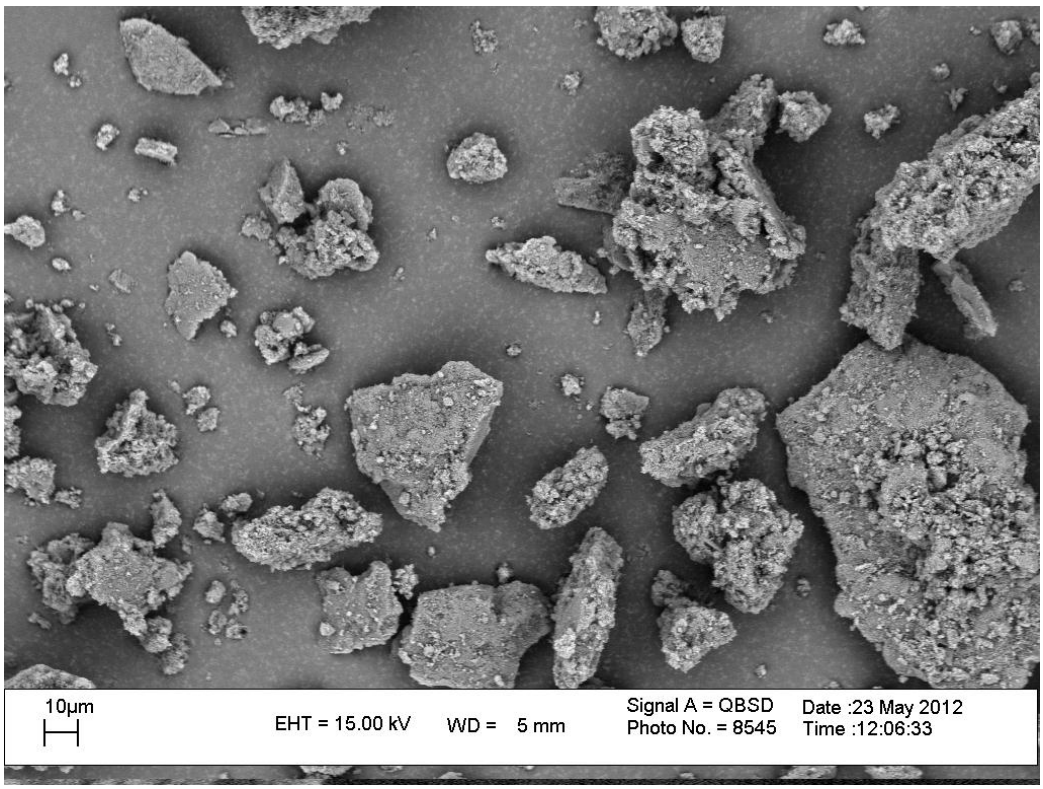
f

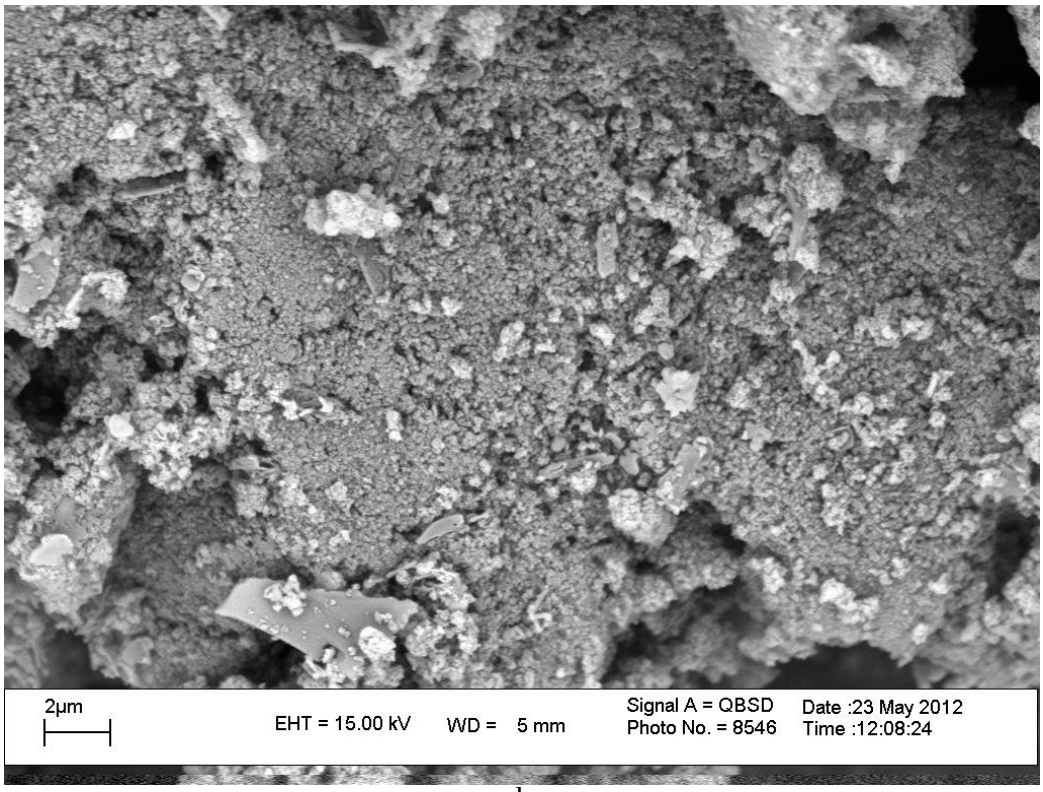


g

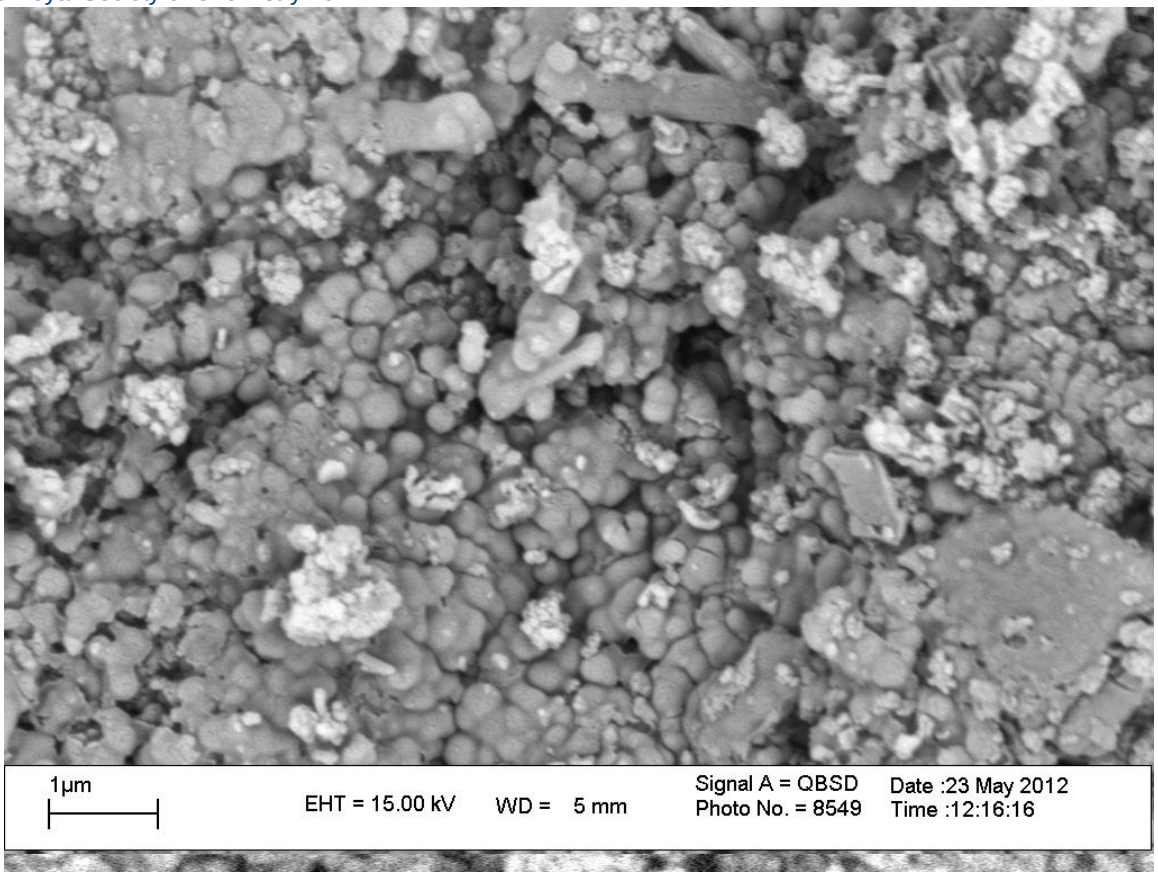
Fig. S2 SEM images of colloidal Birnessite monosheets (a-g).



a



b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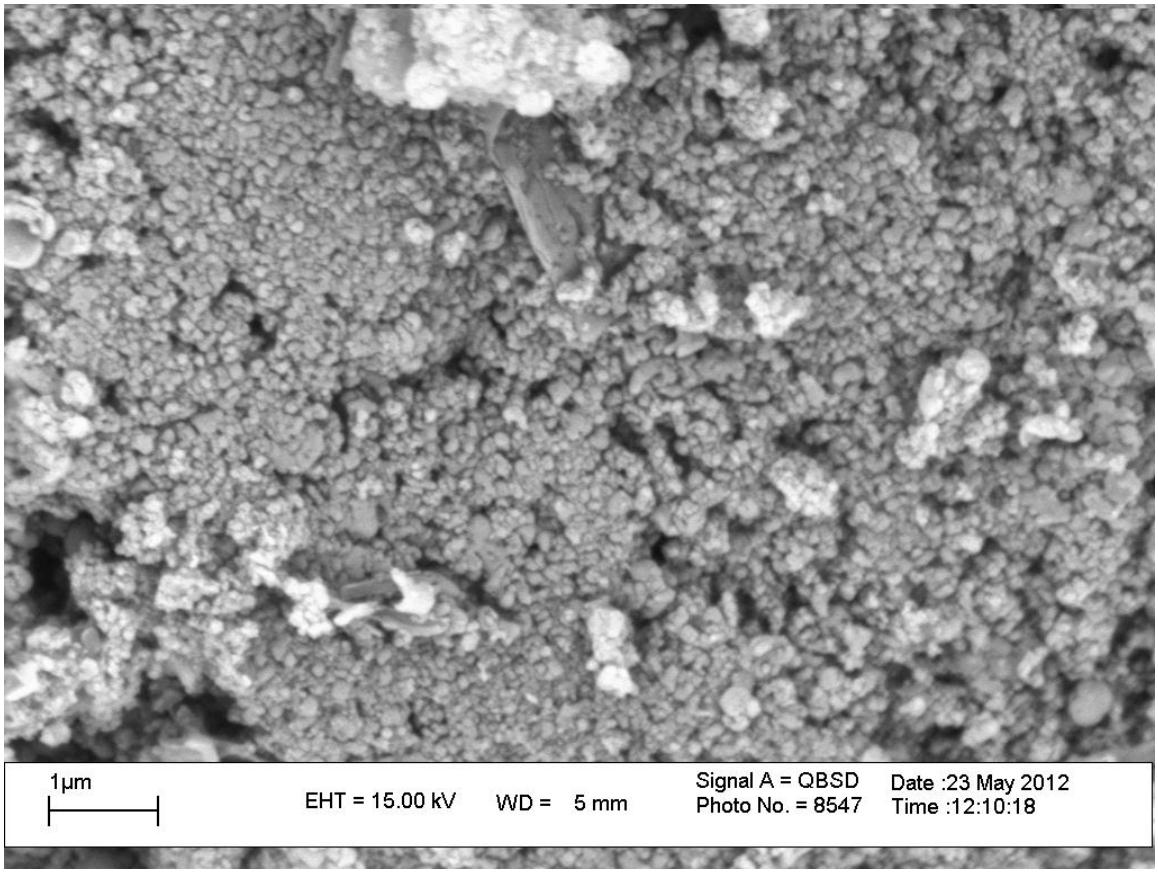
c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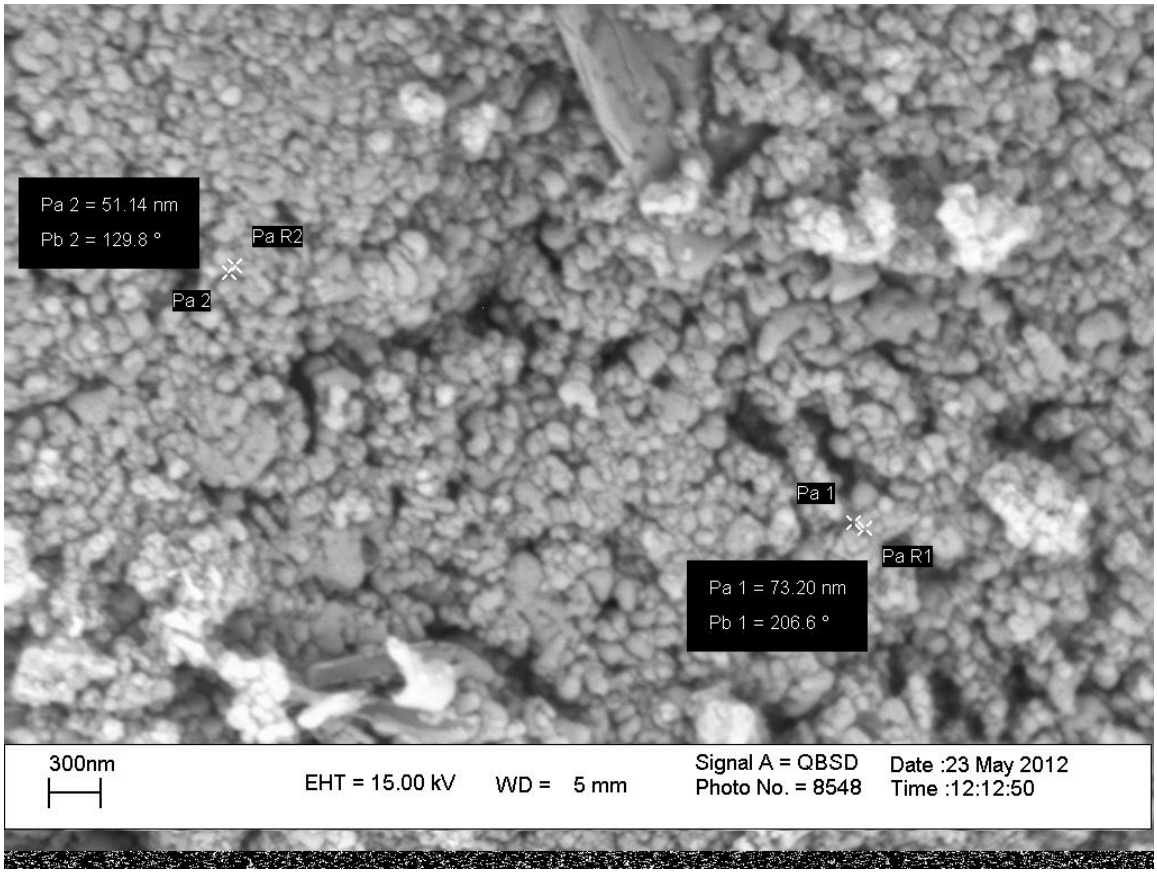
d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Pb 2 = 129.8 °
Pa R2
Pa 2
Pa 1
Pa R1
Pa 1 = 73.20 nm
Pb 1 = 206.6 °
300nm
EHT = 15.00 kV
WD = 5 mm
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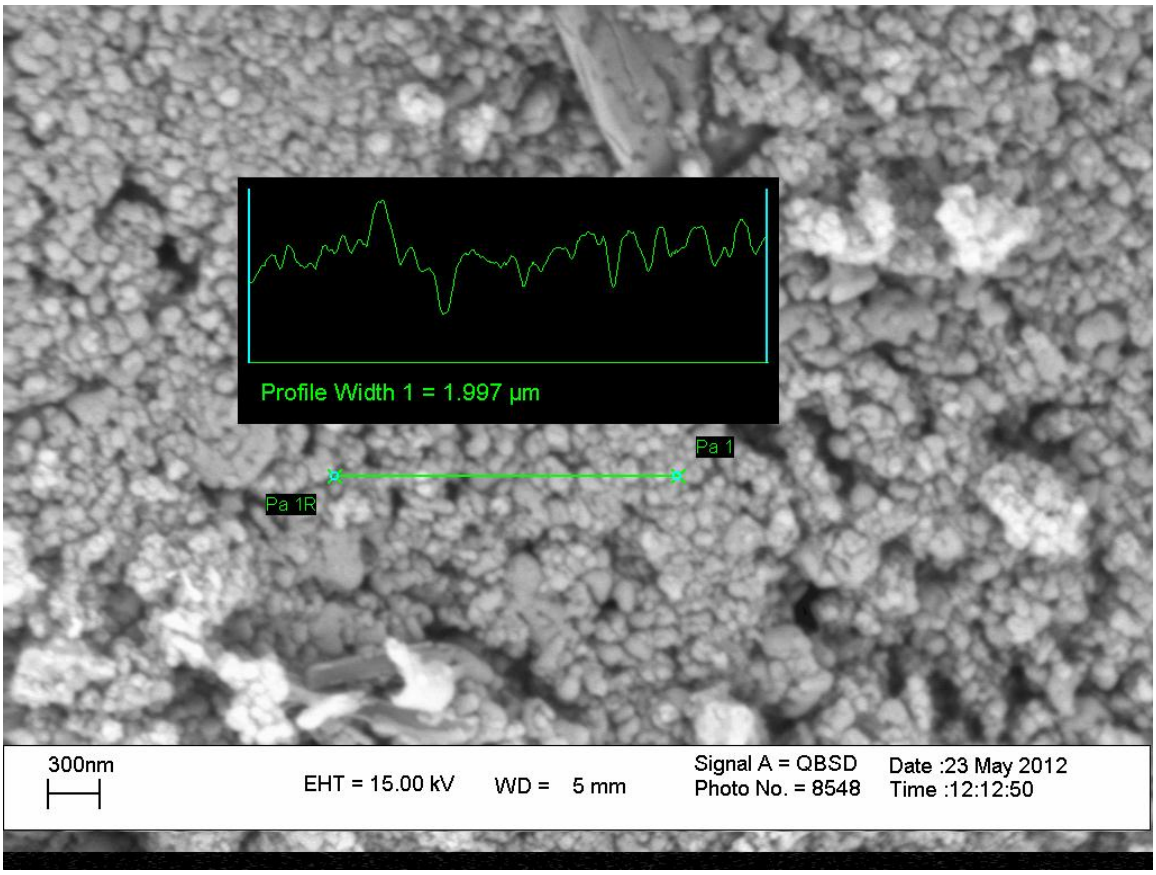
e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Pa 1
Pa 1R
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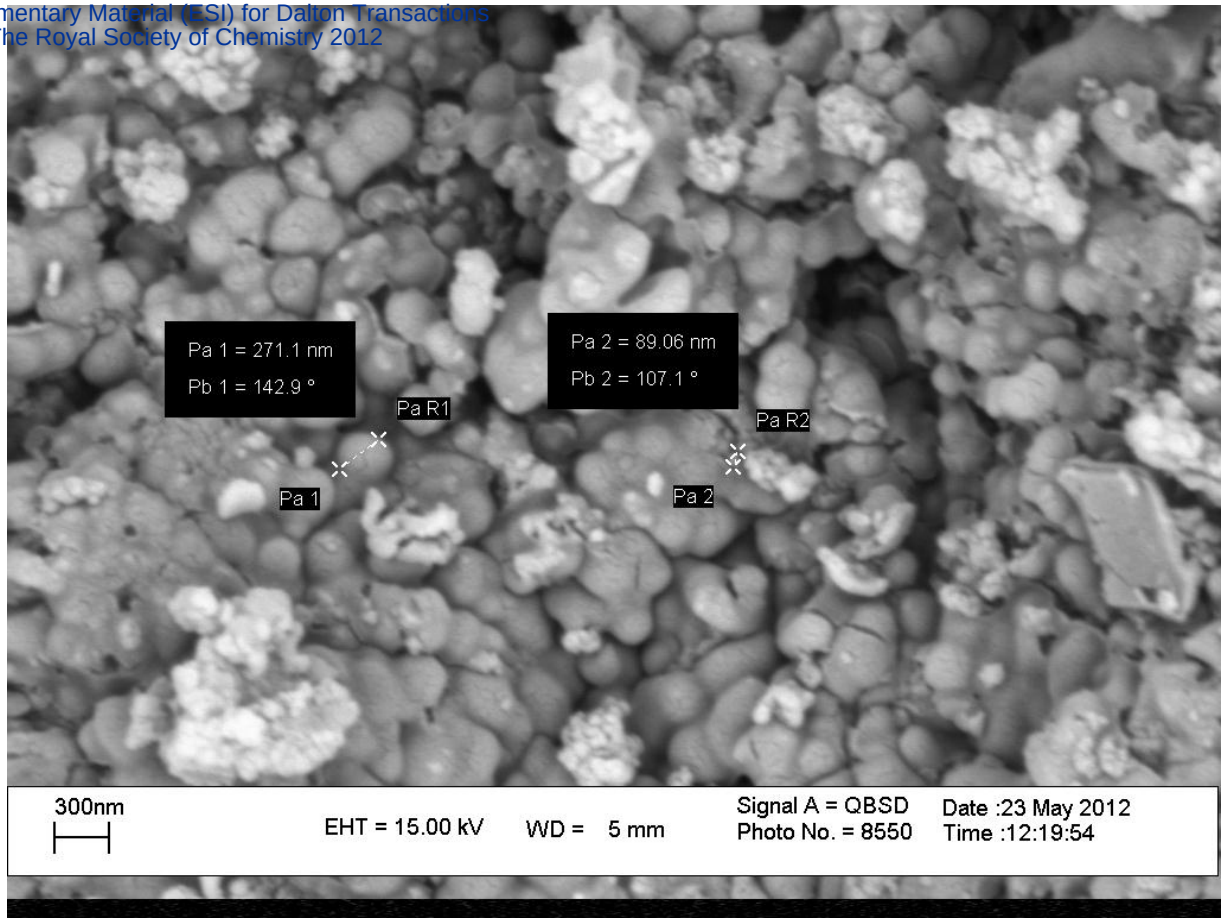
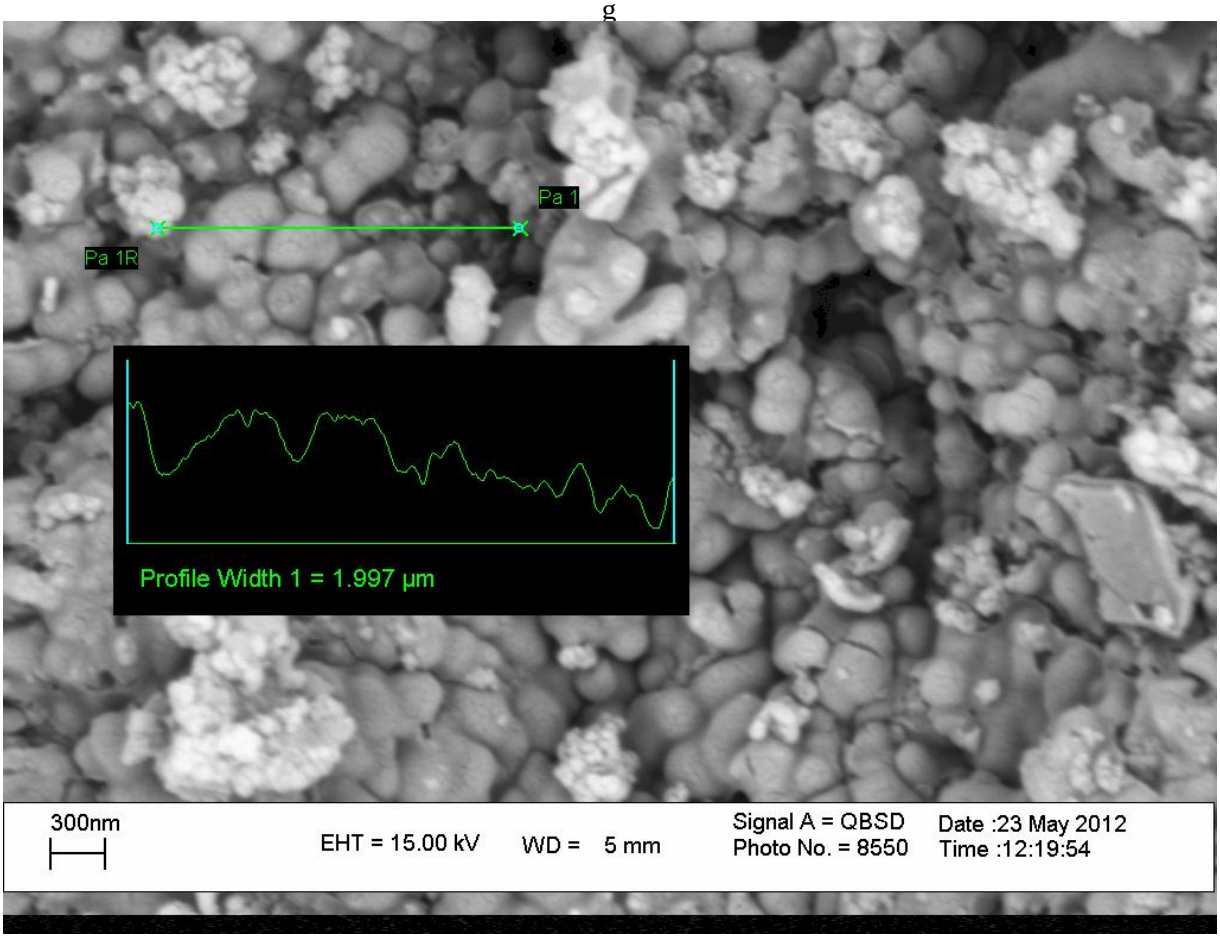
f



g



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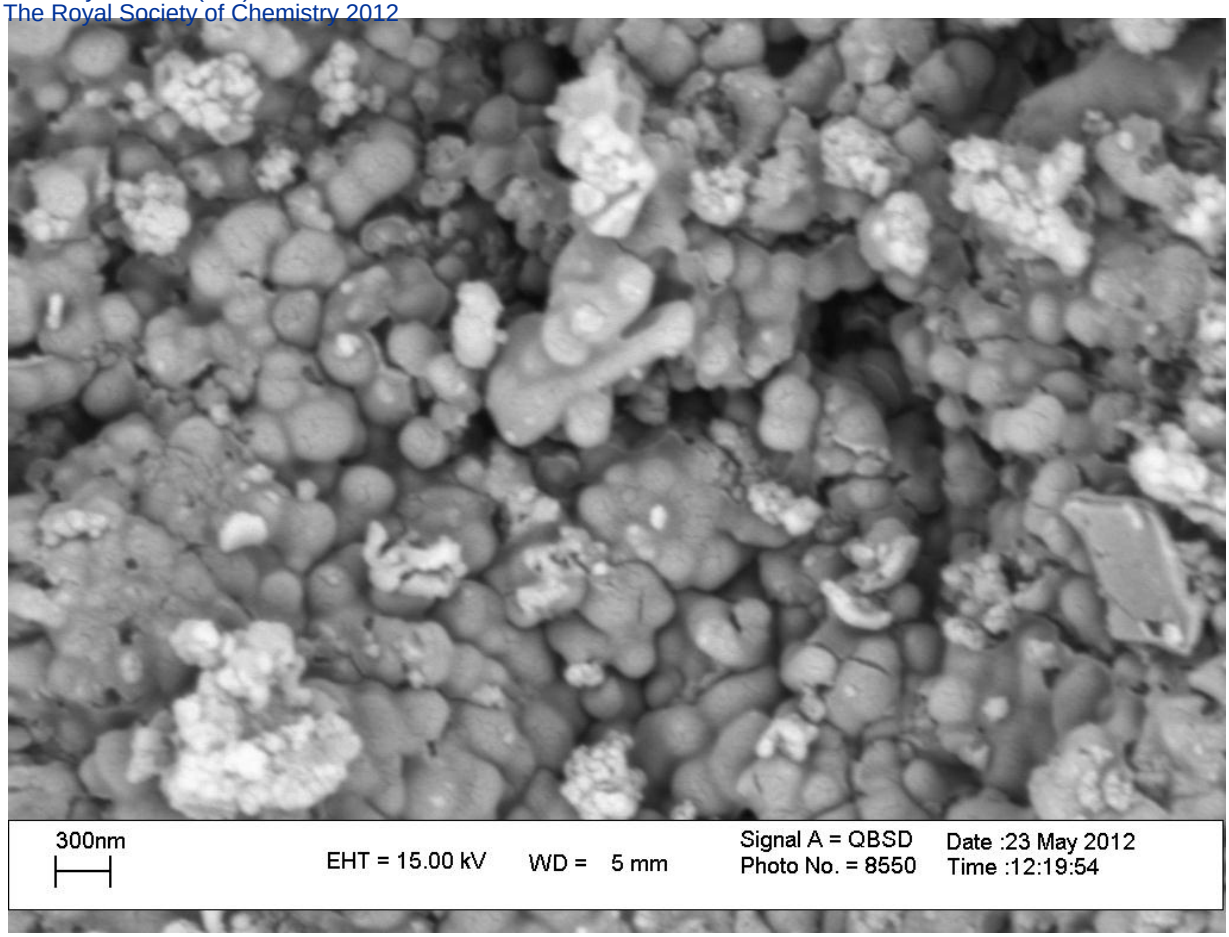
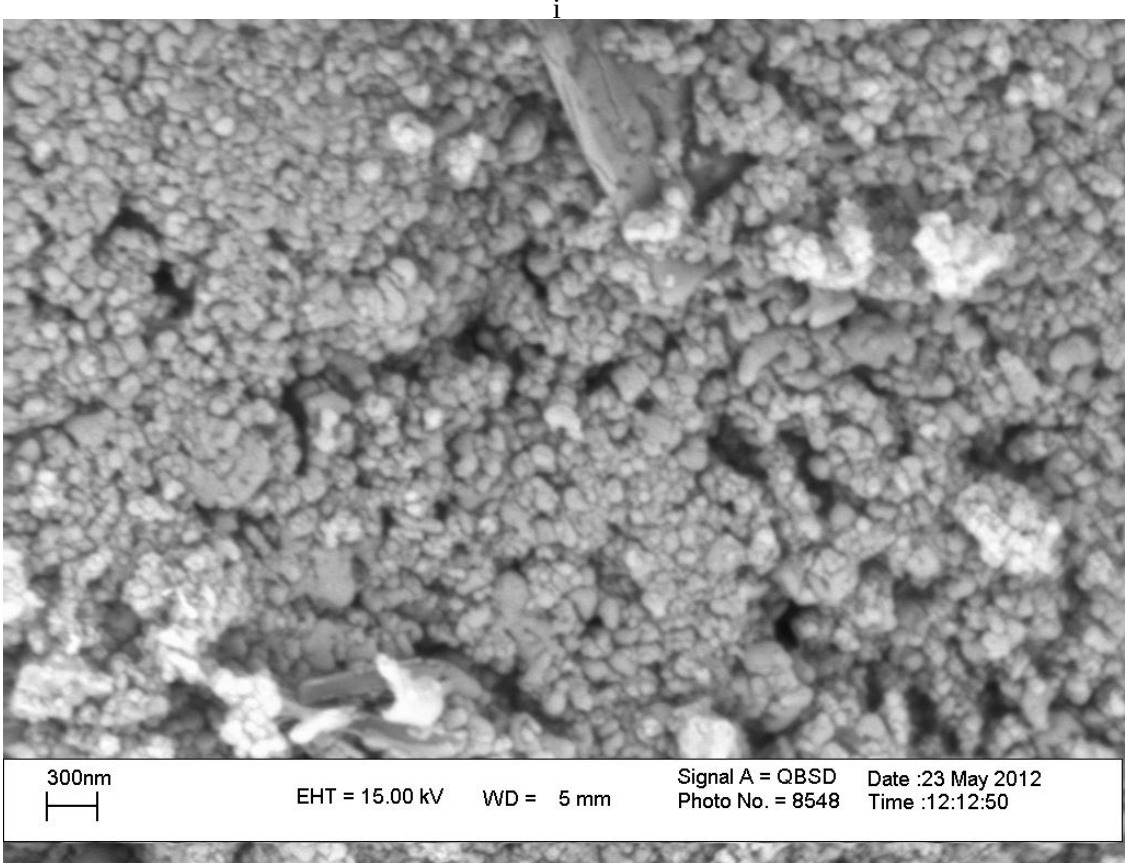


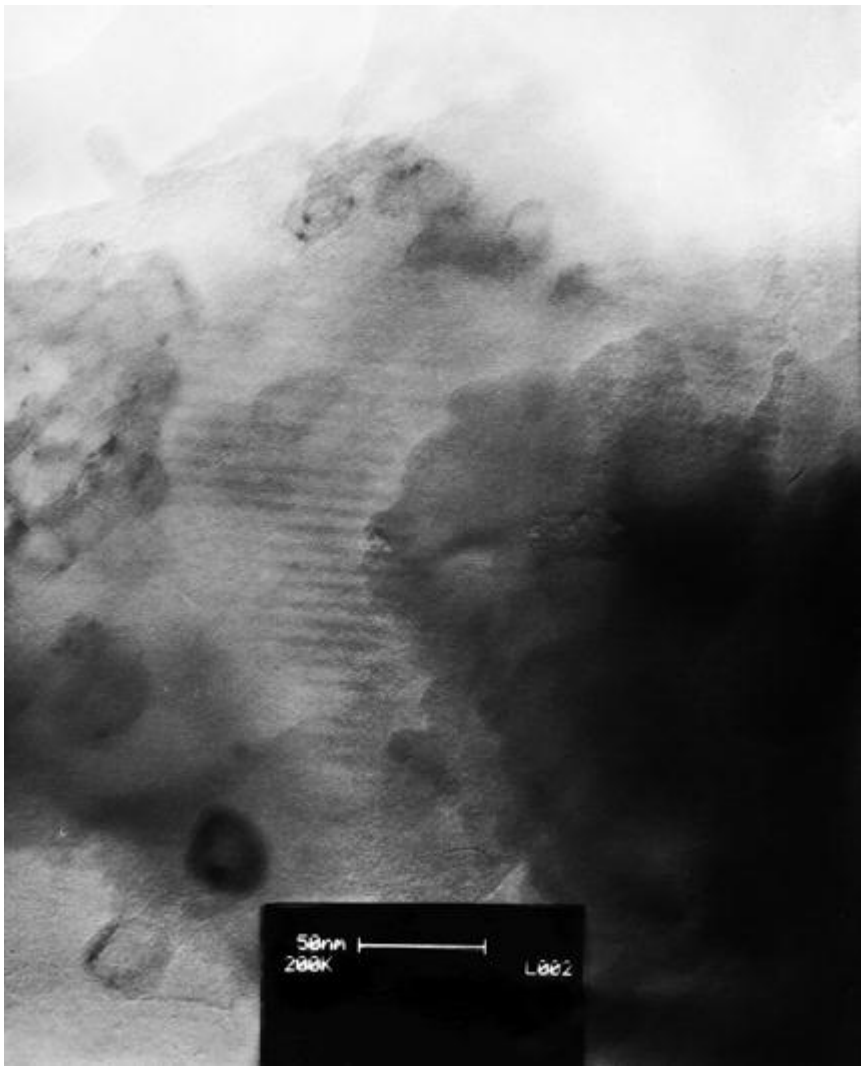
i



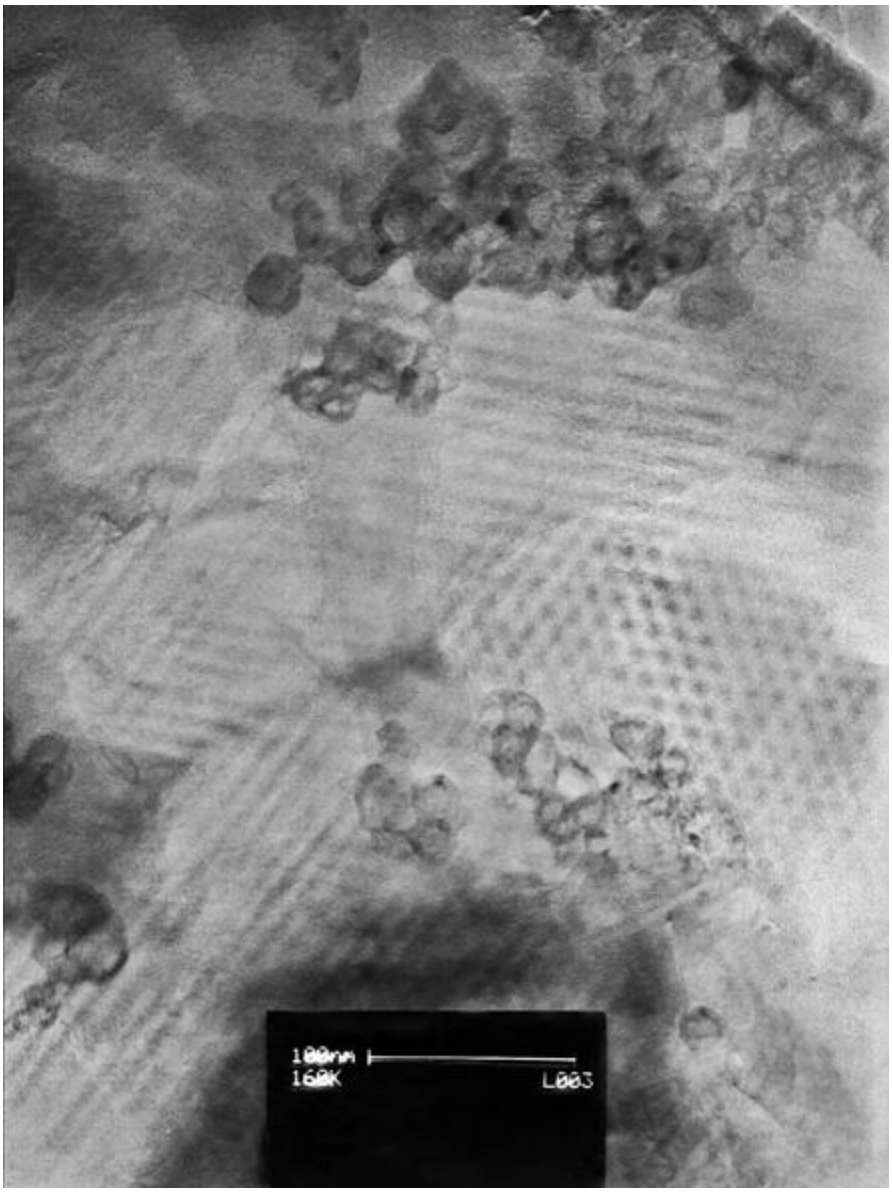
j

Fig. S3 SEM images of model compound **1** (a-j).

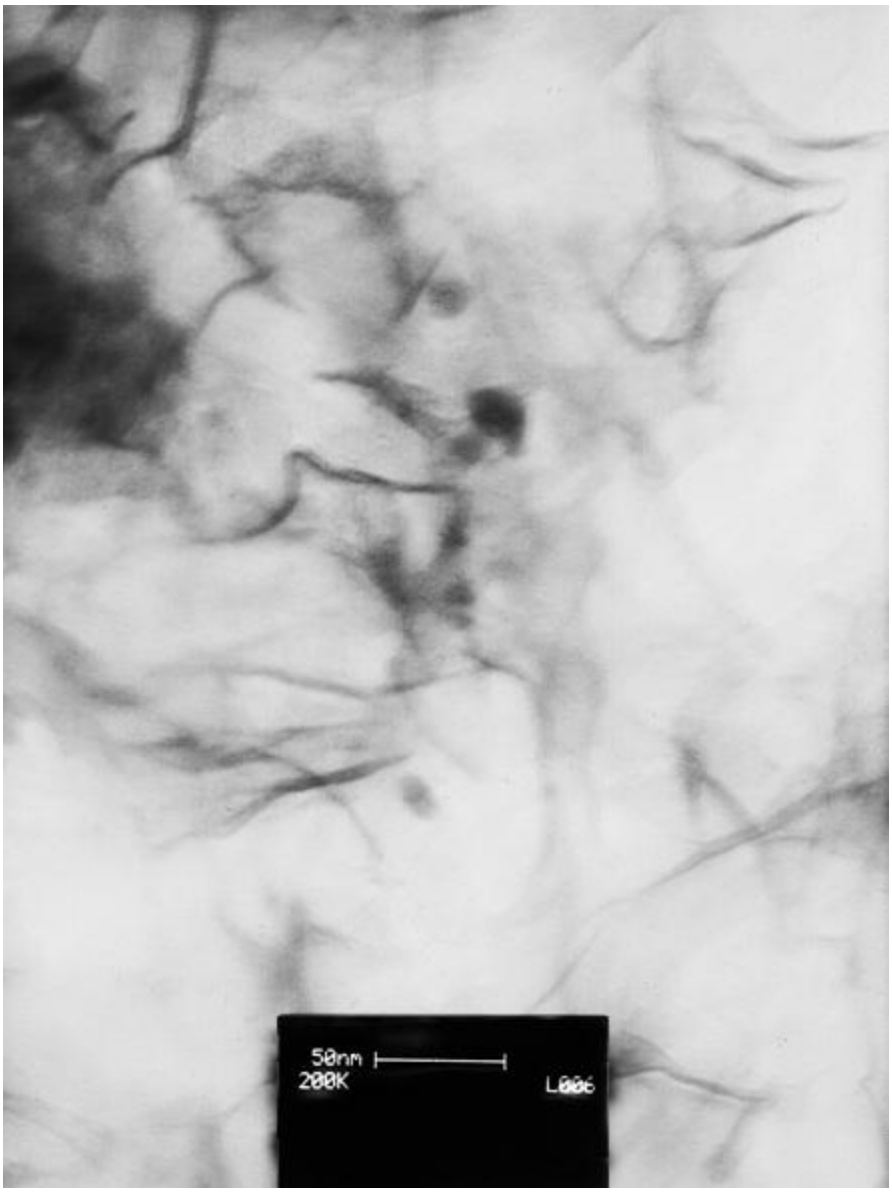
a



b

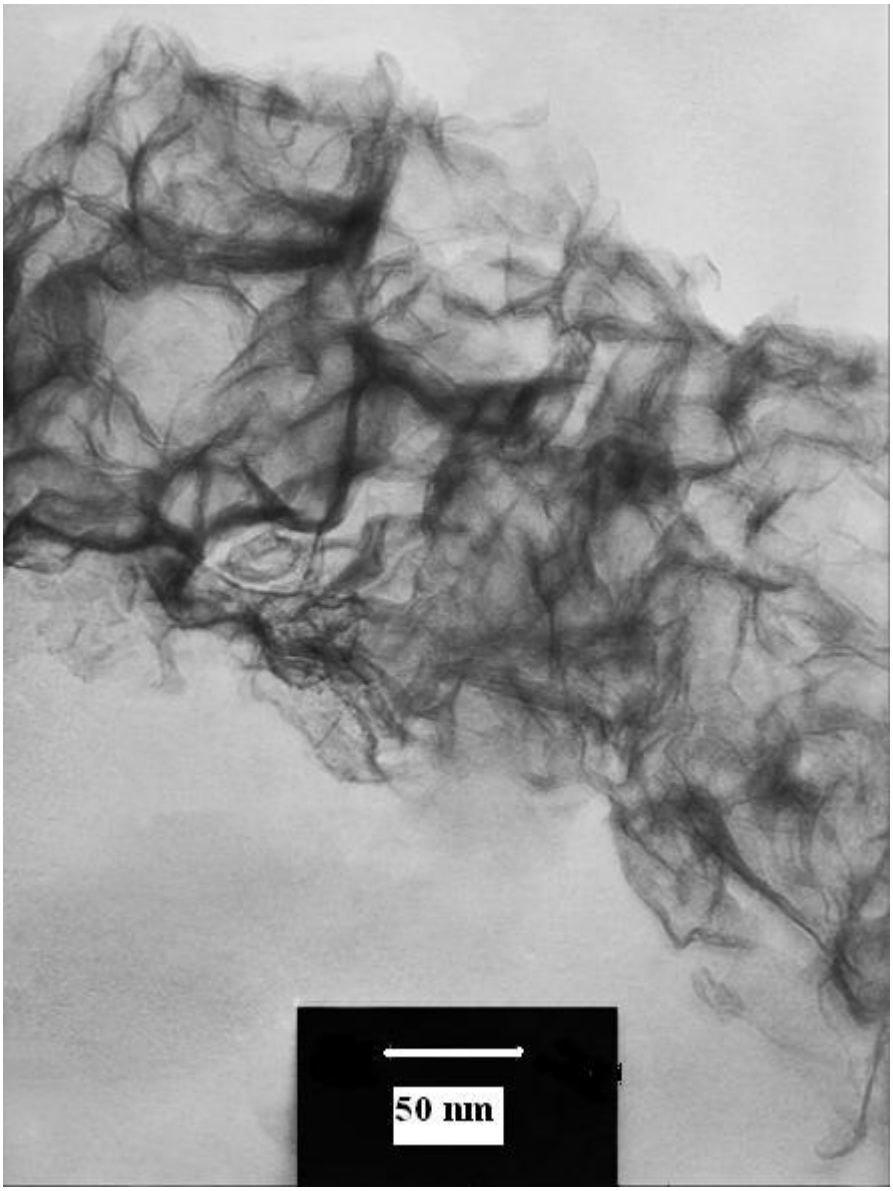


c

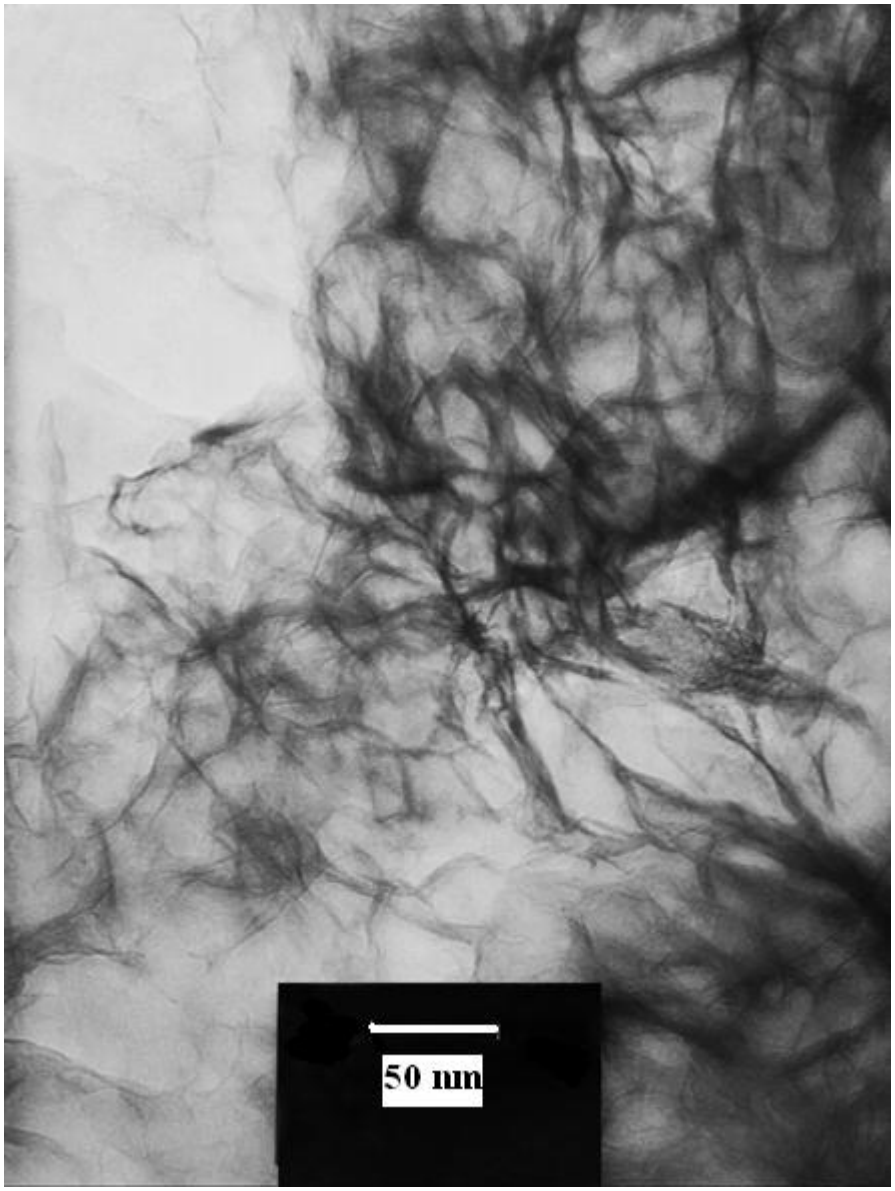


d

Fig. S4 TEM images of colloidal Birnessite monosheets (a-d).



a



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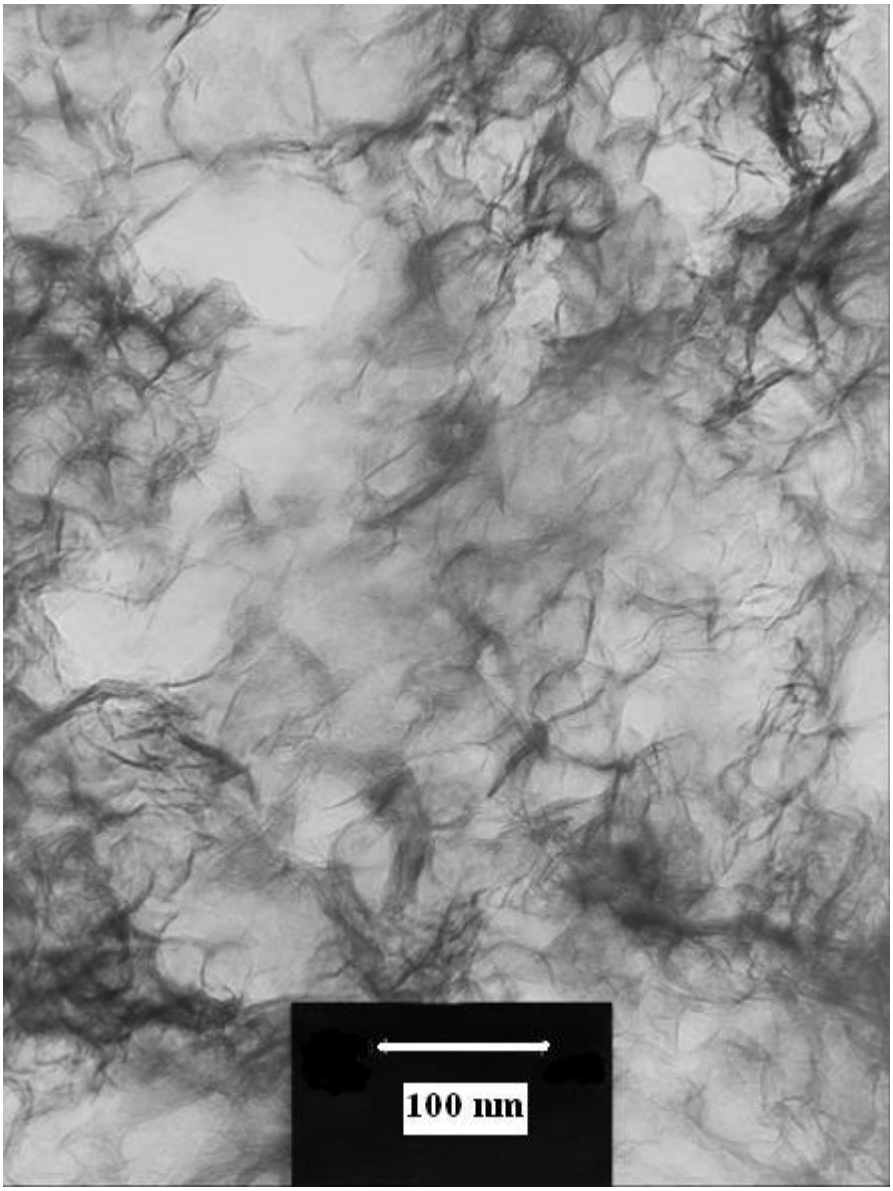
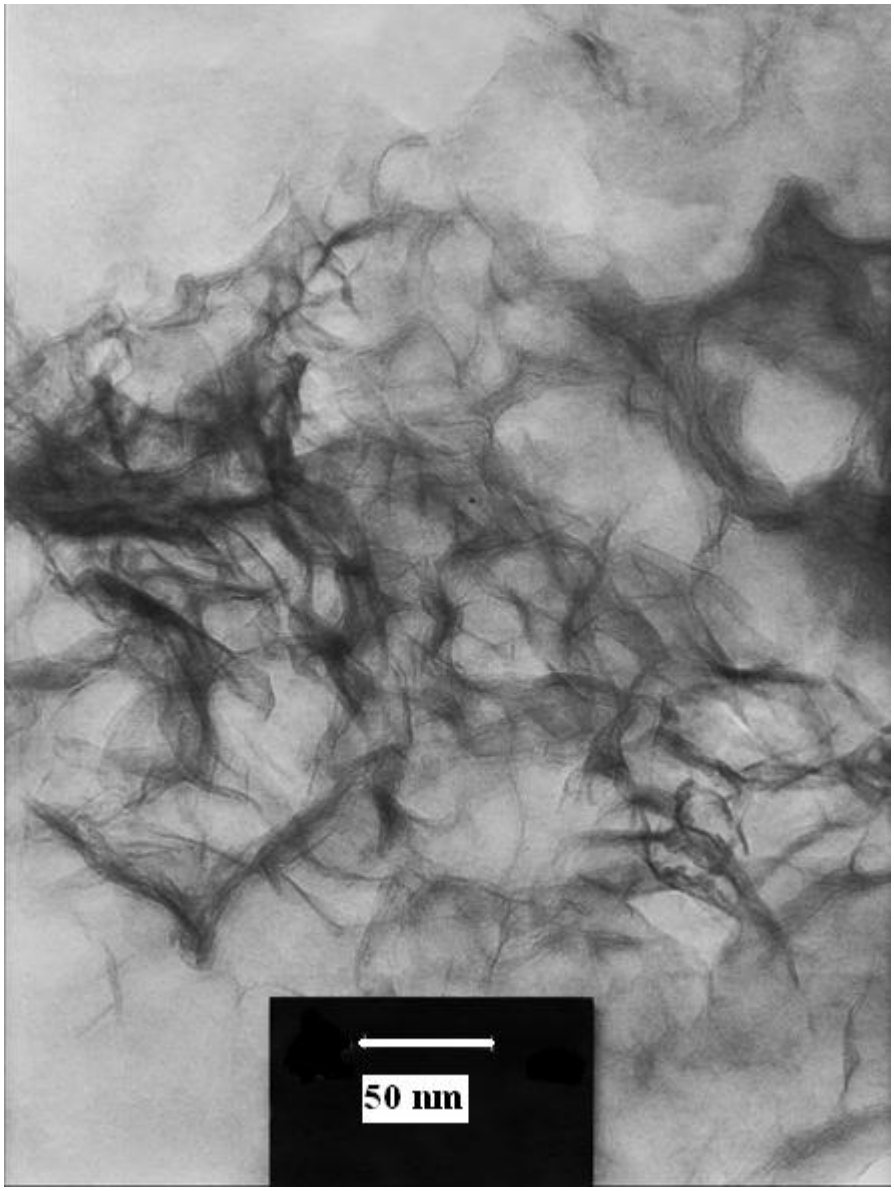
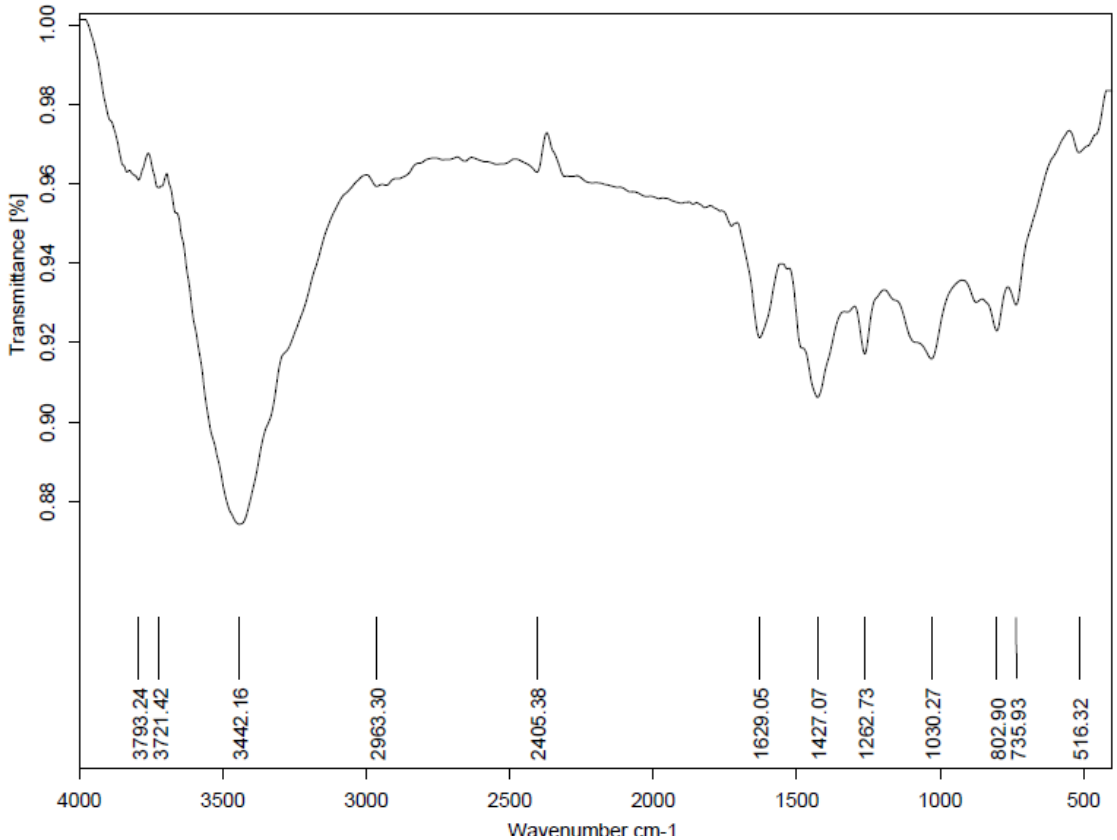


c

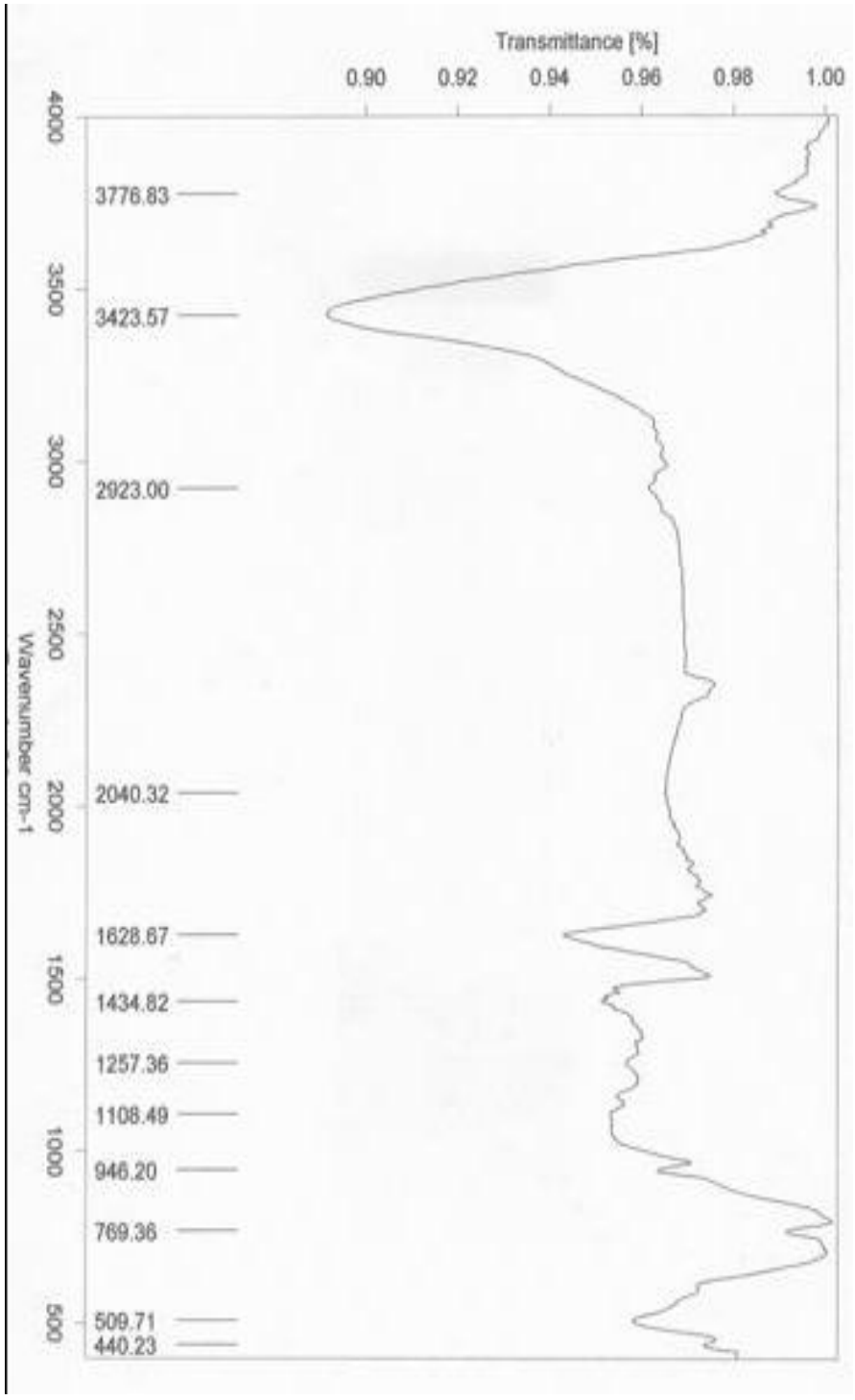


d

Fig. S5 TEM images of model compound **1 (**a-e**)**.



a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0.94
0.96
0.98
1.00
Wavenumber cm-1
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3500
3000
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500
3776.83
3423.57
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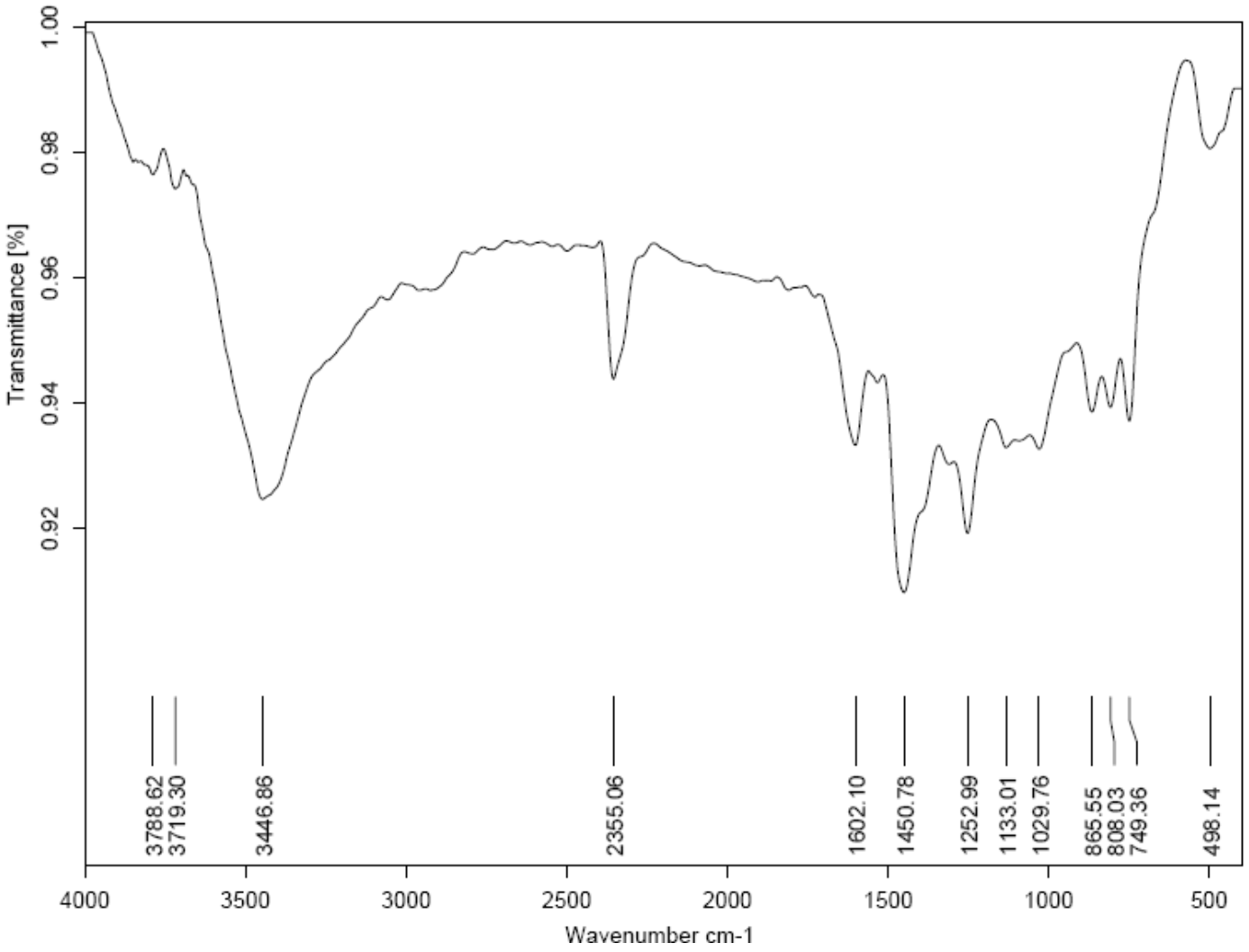
769.36
509.71
440.23

b



c

Fig. S6 MIR of IP (a), manganese (III, IV) oxide monosheet (b), and **1** (c). IR spectrum of **1** indicates the presence of both manganese oxide and IP in the structure.

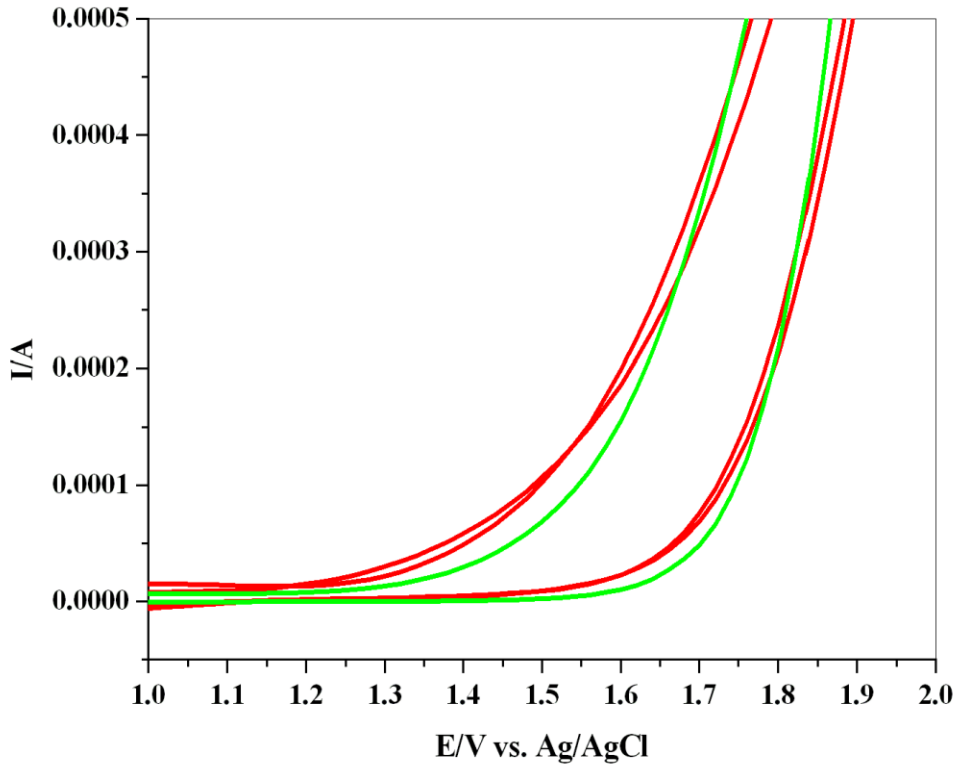


Fig. S7 Cyclic voltammograms of a Pt electrode (green) and Pt (red) electrode modified with dried manganese (III, IV) oxide monosheets in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 50 mV. s^{-1}.

Reference:

1. K. Kai, Y. Yoshida, H. Kageyama, G. Saito, T. Ishigaki, Y. Furukawa, J. Kawamata, *J. Am. Chem. Soc.* 2008, **130**, 15938-15943.