

Supplementary Information

A manganese oxide with phenol groups as a promising structural model for water oxidizing complex in Photosystem II: A ‘Golden fish’

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Methods

All reagents and solvents were purchased from commercial sources and were used without further purification. MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400 and 4000 cm^{-1} . The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-K α radiation). Manganese atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer Varian Spectr AA 110. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. Prior to the analysis, the oxides (10.0 mg metal) were added to 1 mL of concentrated nitric acid and H₂O₂, left at room temperature for at least 1 h to ensure that the oxides were completely dissolved. The solutions were then diluted to 25.0 mL and analyzed by AAS. 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 **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 electrodes, 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 H₂O₂ was added to 10 mL of 0.3 M MnCl₂·4H₂O 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 1:

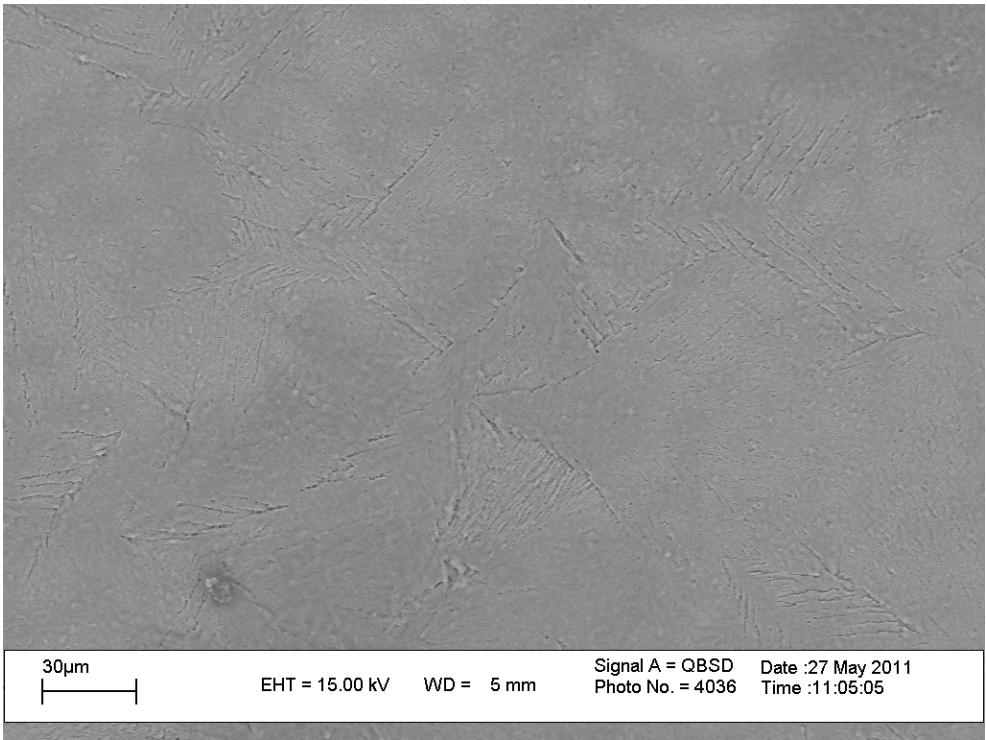
4 - aminophenol (245 mg, 2.25 mmol) was dissolved (at pH ~ 6, using glacial acetic acid) in 10 mL water and the solution was added to 50 mL of the colloidal suspension of MnO₂ monosheets (4 mM) during argon bubbling at room temperature. Immediately after the addition, flocculation occurred in the mixed solution. The resulting brown precipitate was filtered off, washed with water, air-dried at room temperature and then dried under vacuum.

The manganese was estimated to be 43.4 % in **1** on the basis of atomic absorption spectroscopy. Anal. Found. For **1**: C, 11.3; H, 2.9; N, 2.2. Atomic absorption spectroscopy and elemental analysis showed that **1** can be formulated as: (4- aminophenol)_{0.2}MnO₂.H₂O.

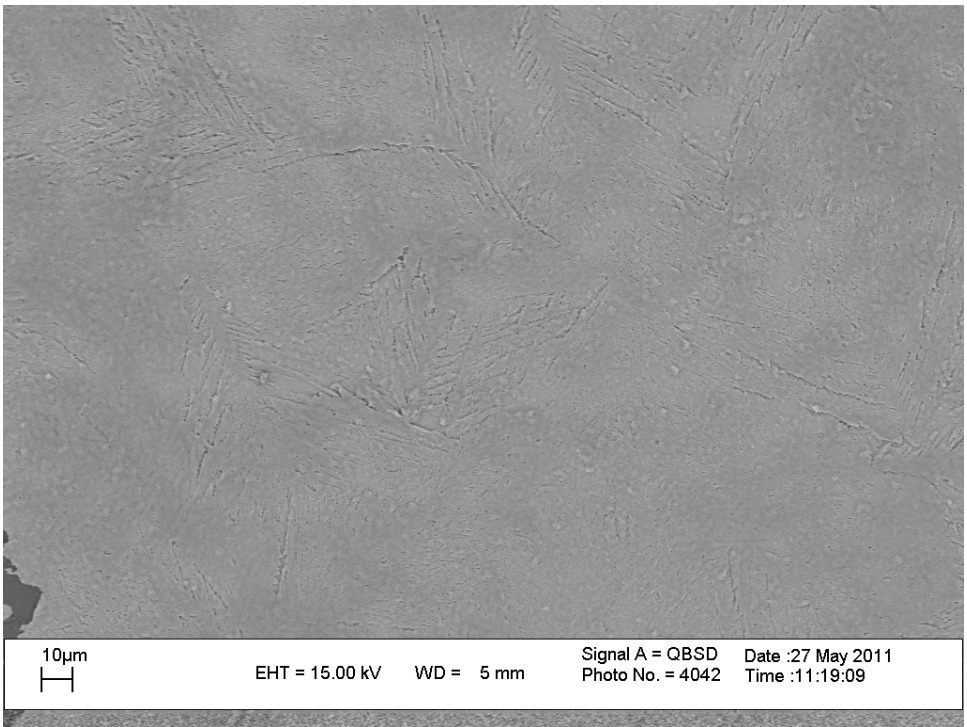
Preparation of modified electrode

A bare glassy carbon electrode was polished with **1**, 0.3 and 0.05μm alumina slurry, respectively, 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 **1** suspension was dispersed, ultrasonically, in water. The modified electrode was prepared by dropping 20μL of **1** suspension (0.1mg.mL⁻¹) on the Pt electrode surface and dried at room temperature. Finally, 10μL of **1** wt % Nafion solution was deposited onto the centre of the modified electrode. The electrochemical

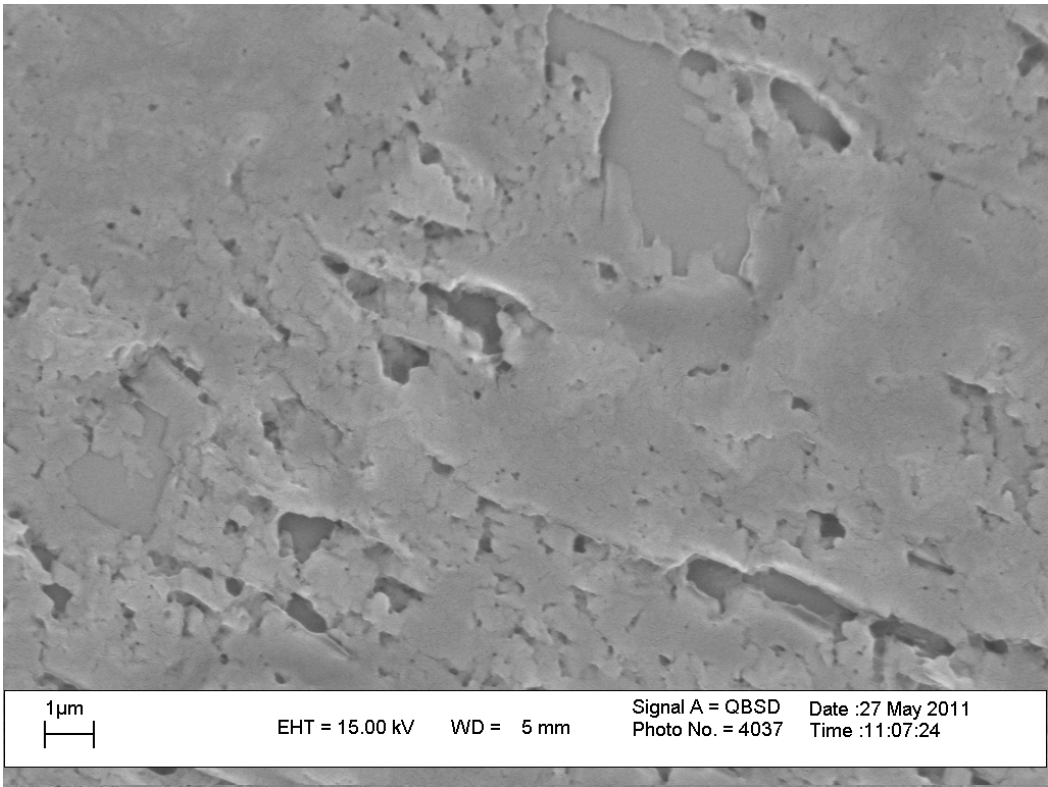
properties of different electrodes were investigated by cyclic voltammetry (CV) in a 0.1M pH 6.3 lithium perchlorate solution.



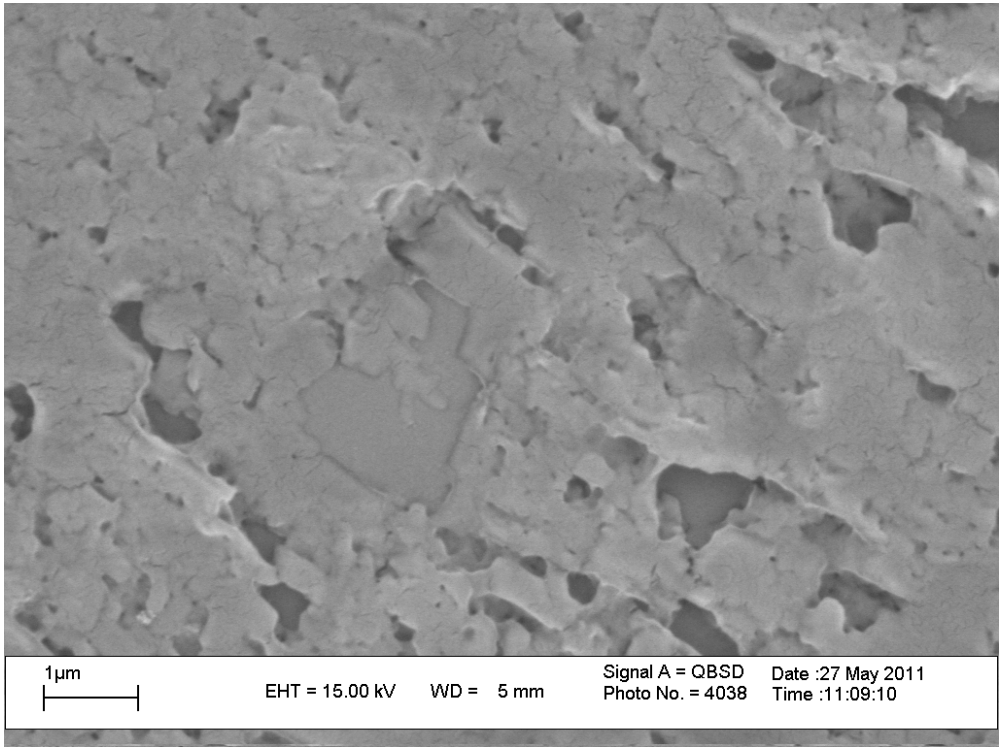
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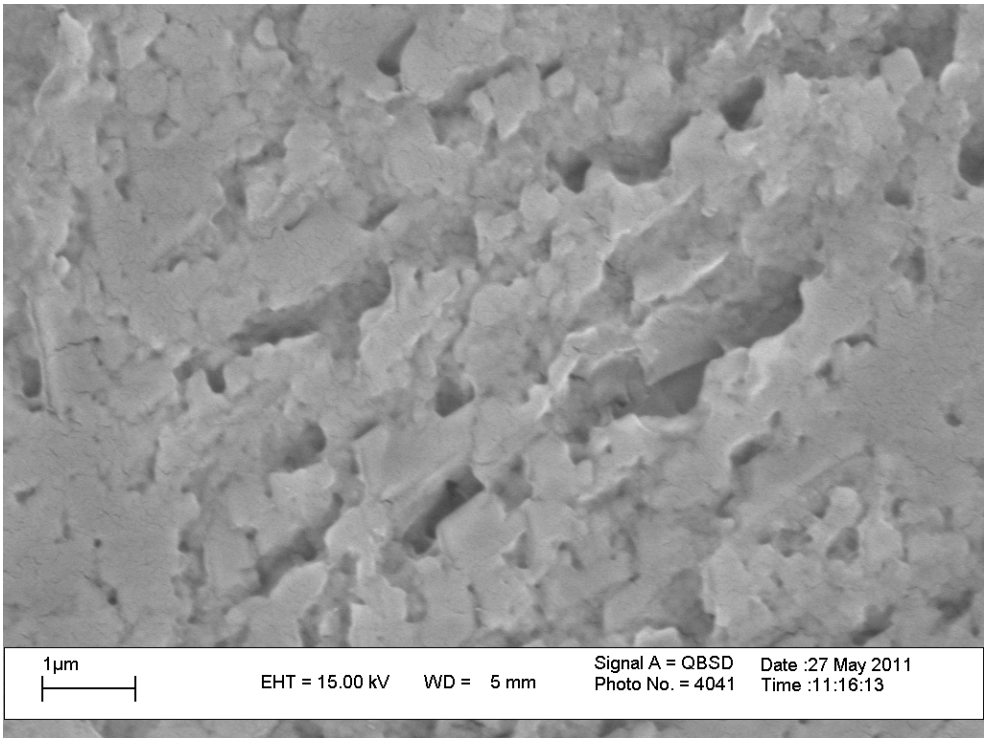
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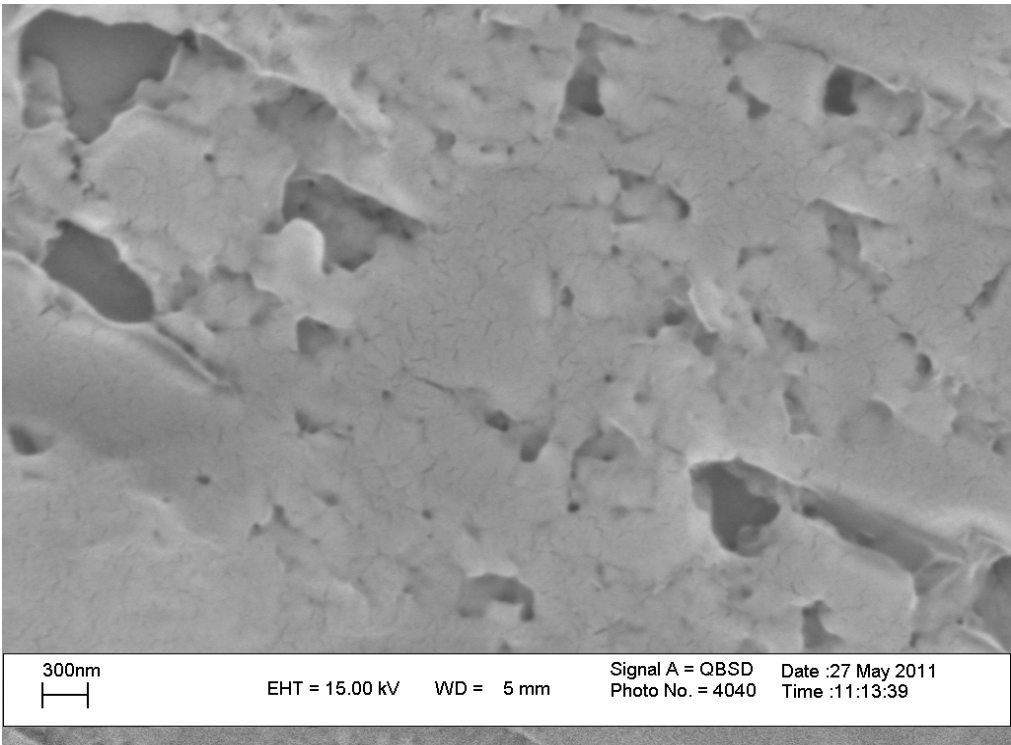
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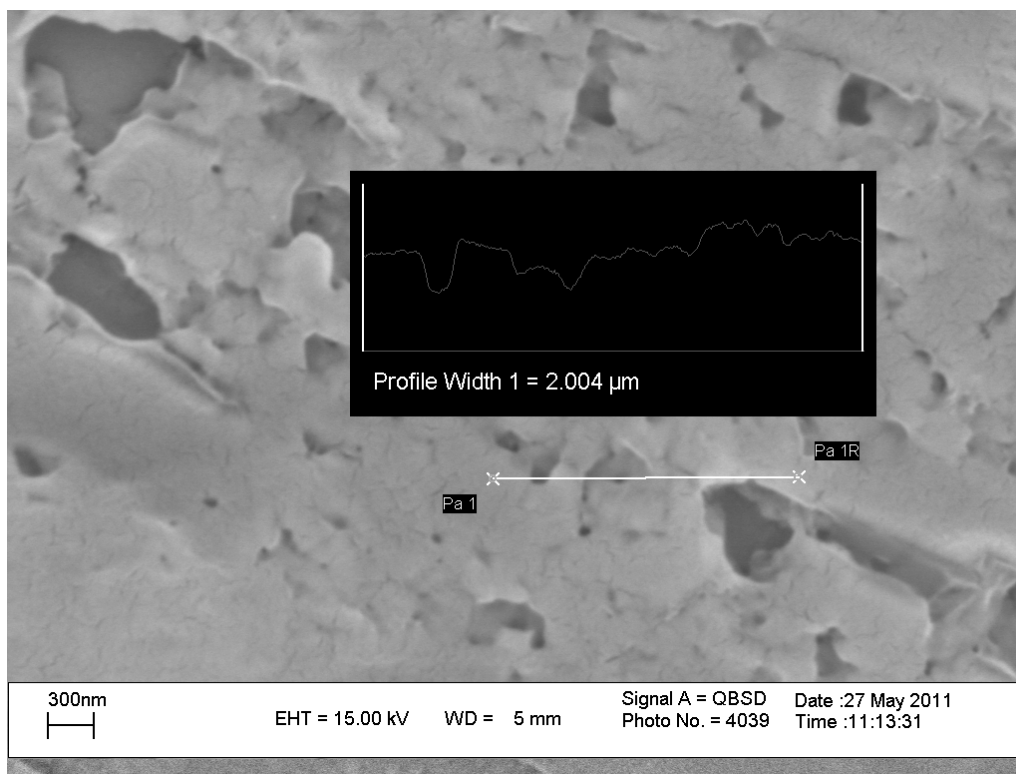
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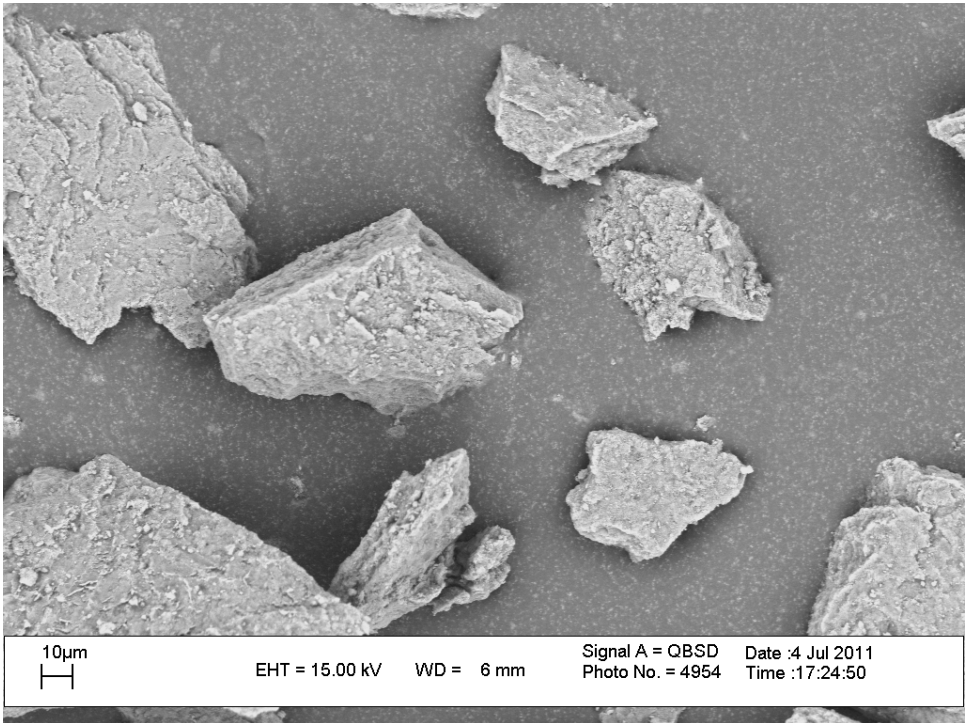


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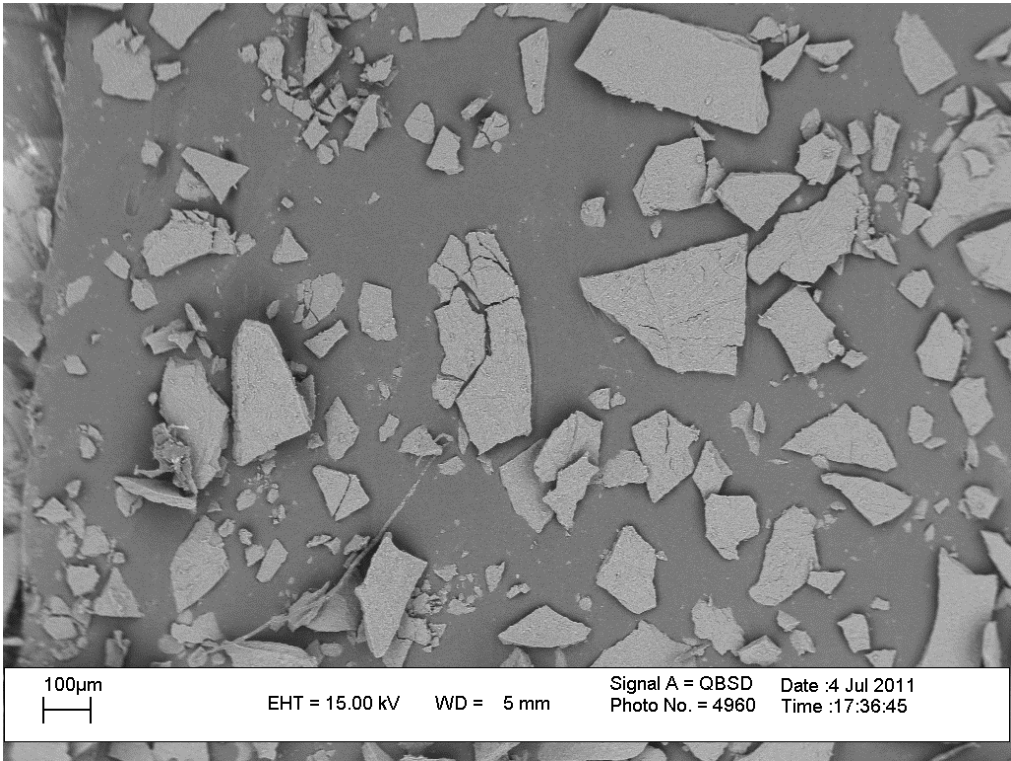


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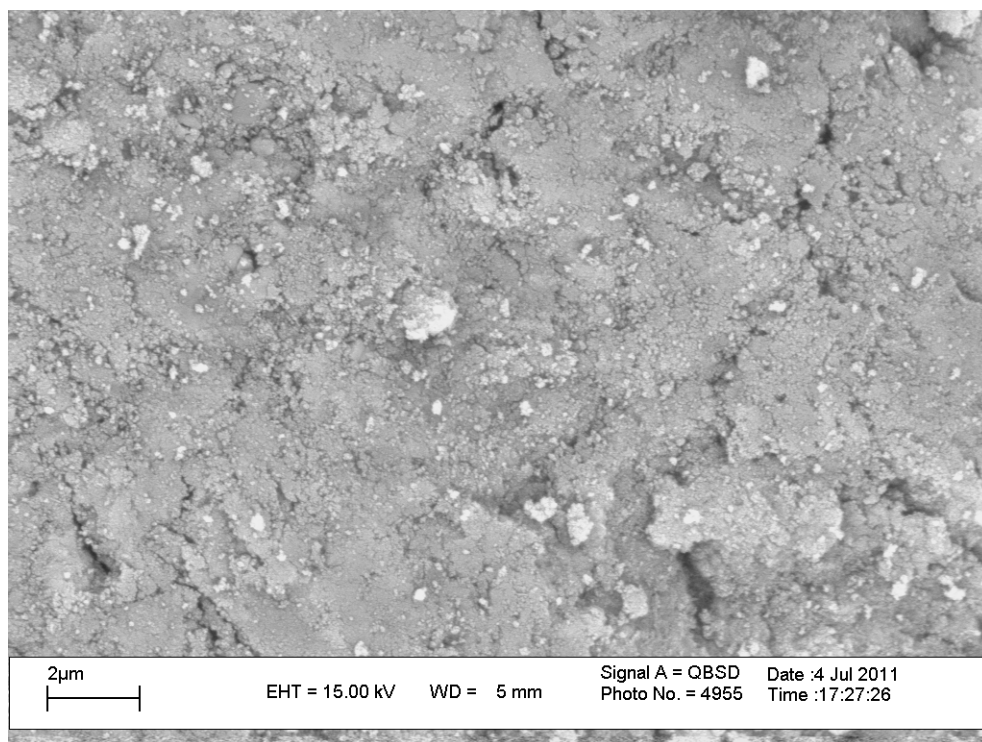
Fig. S1. SEM images of colloidal Birnessite monosheets (a-g).



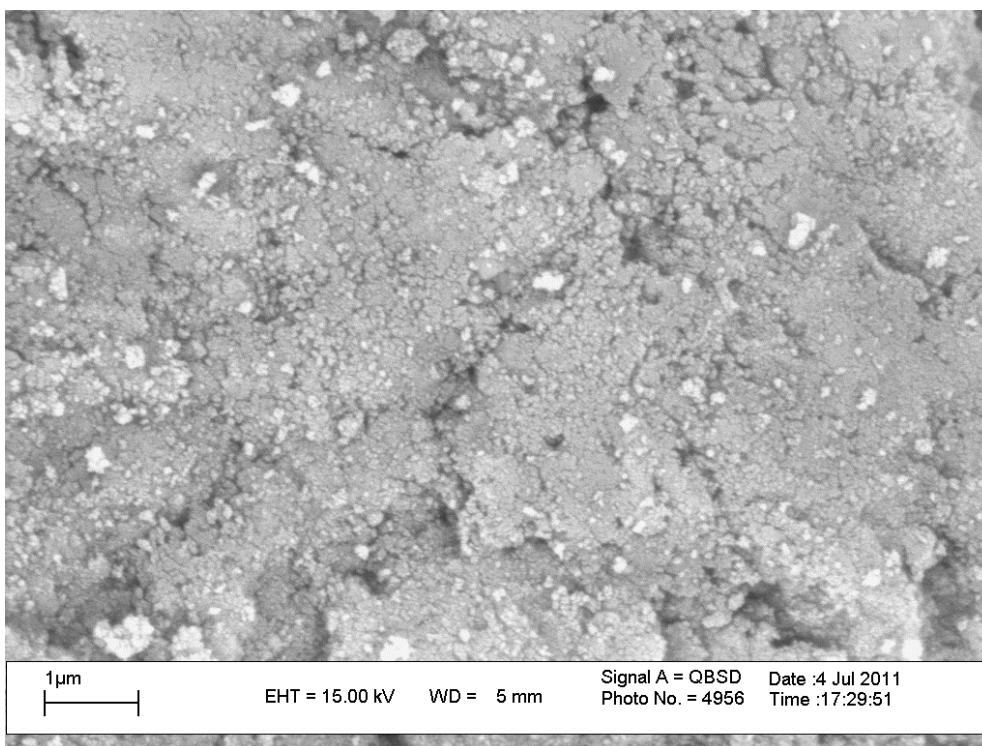
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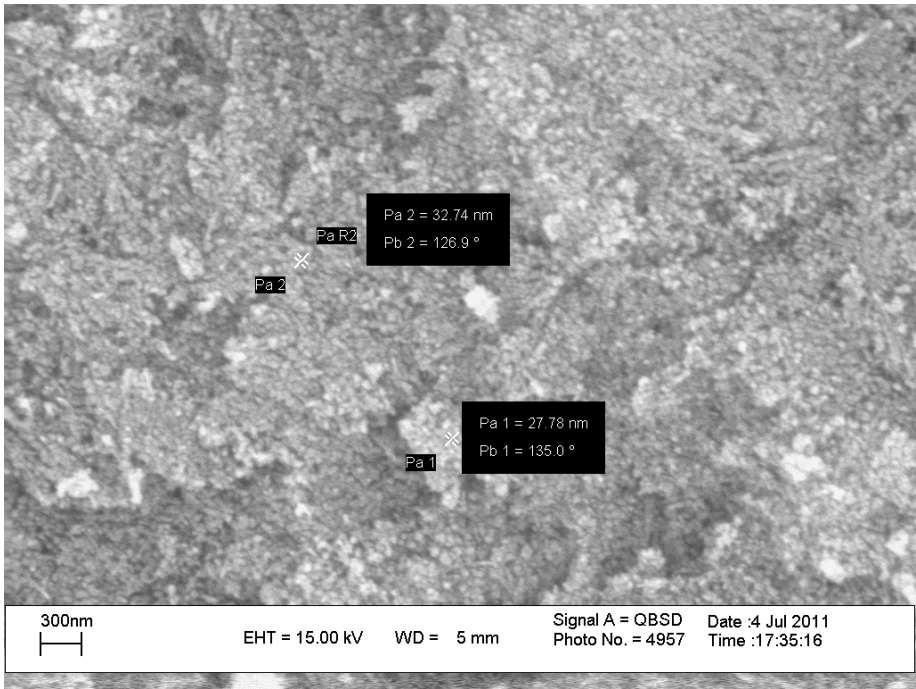
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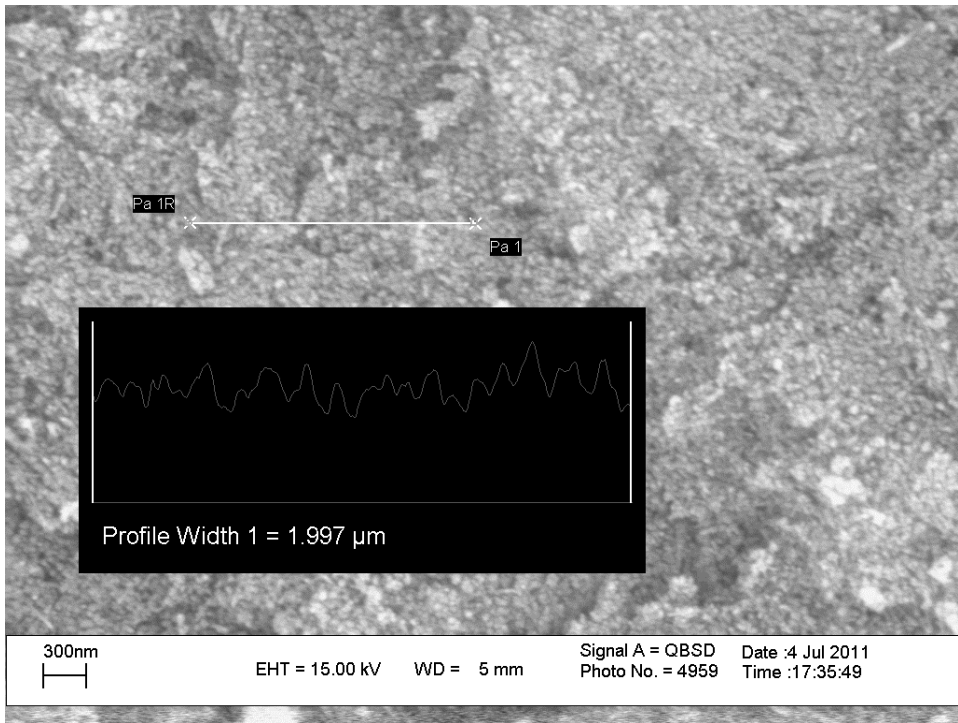
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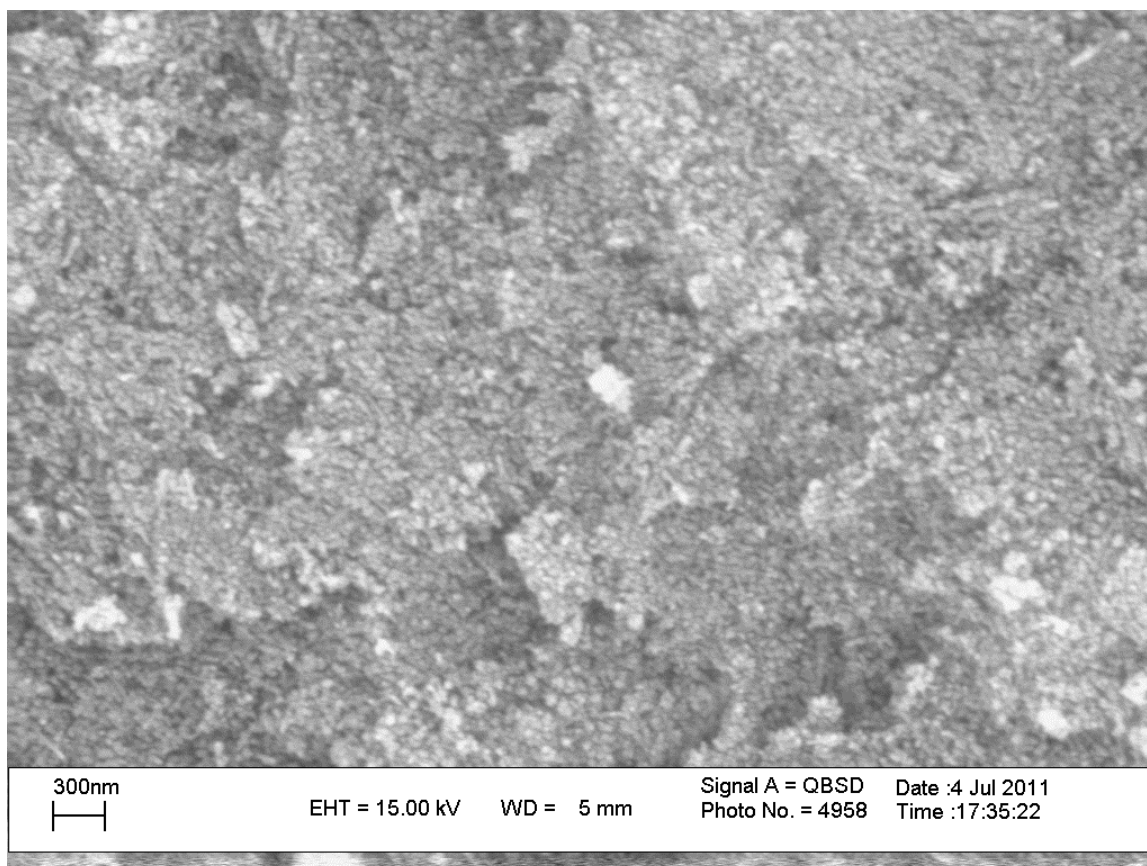
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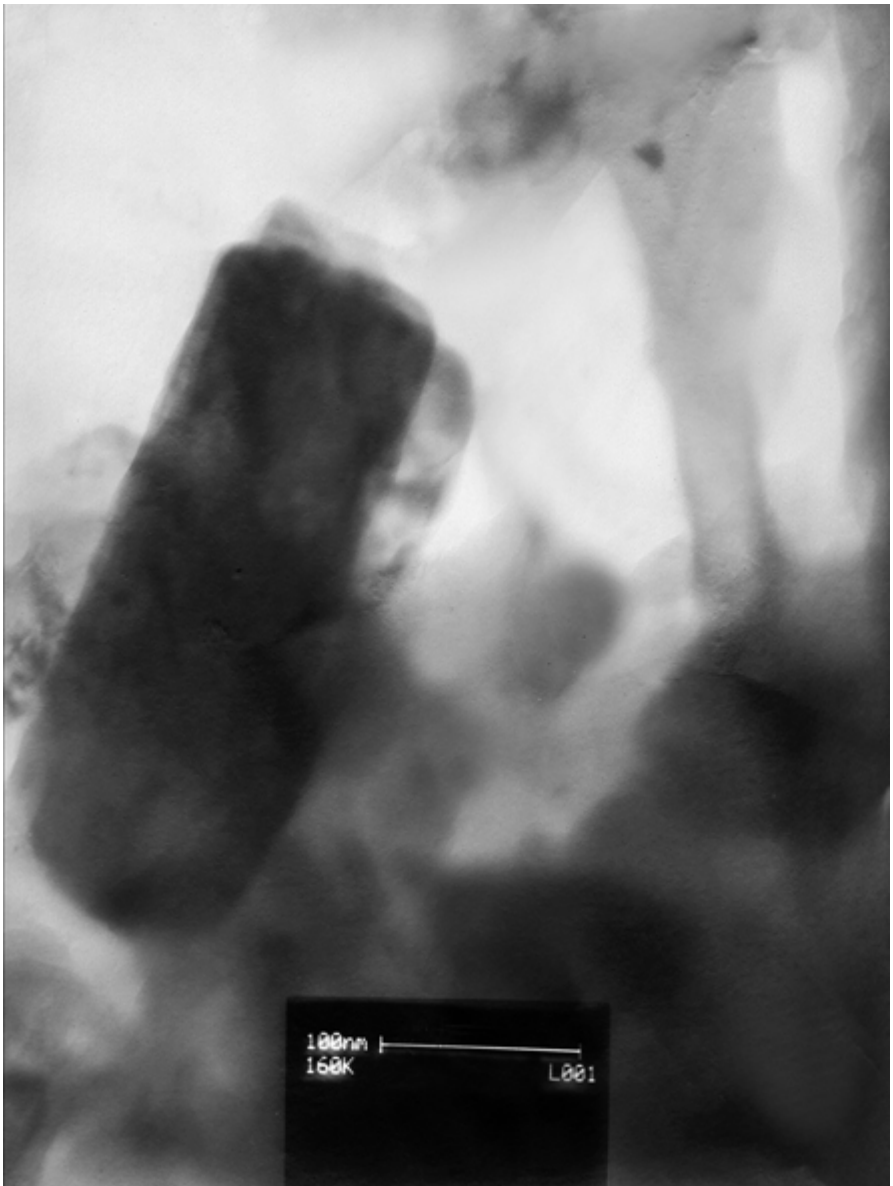


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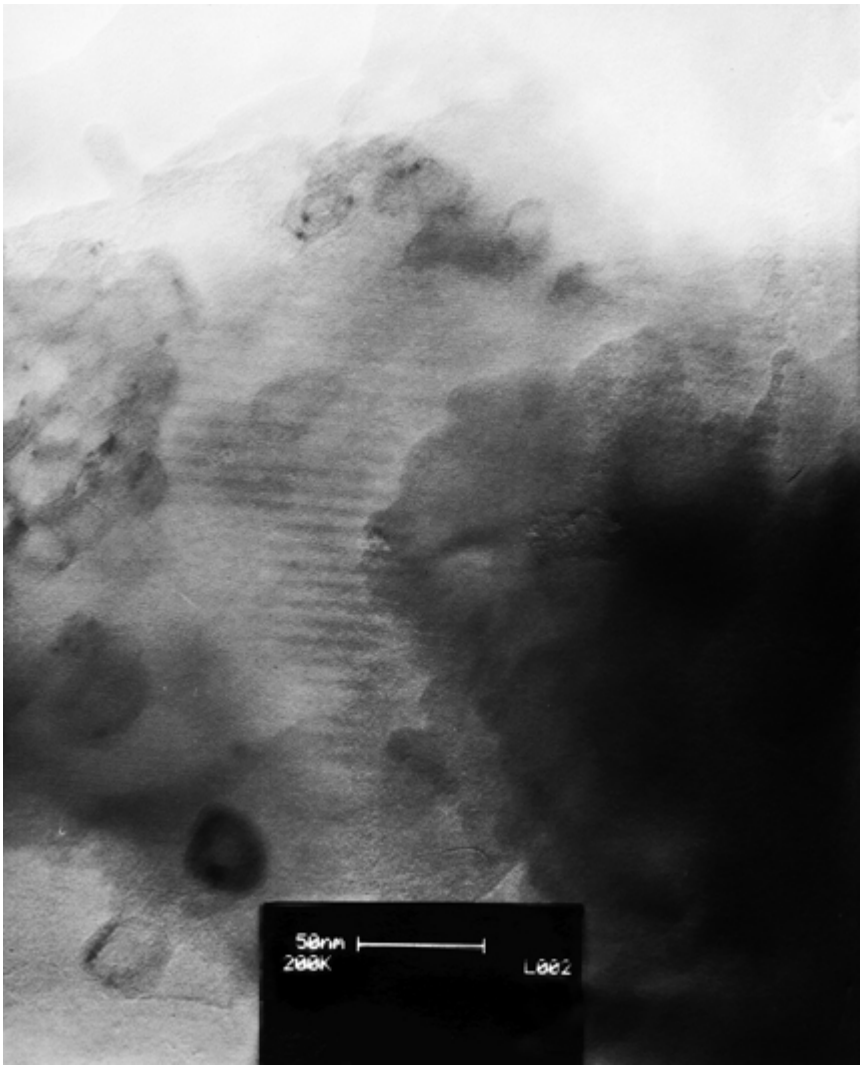


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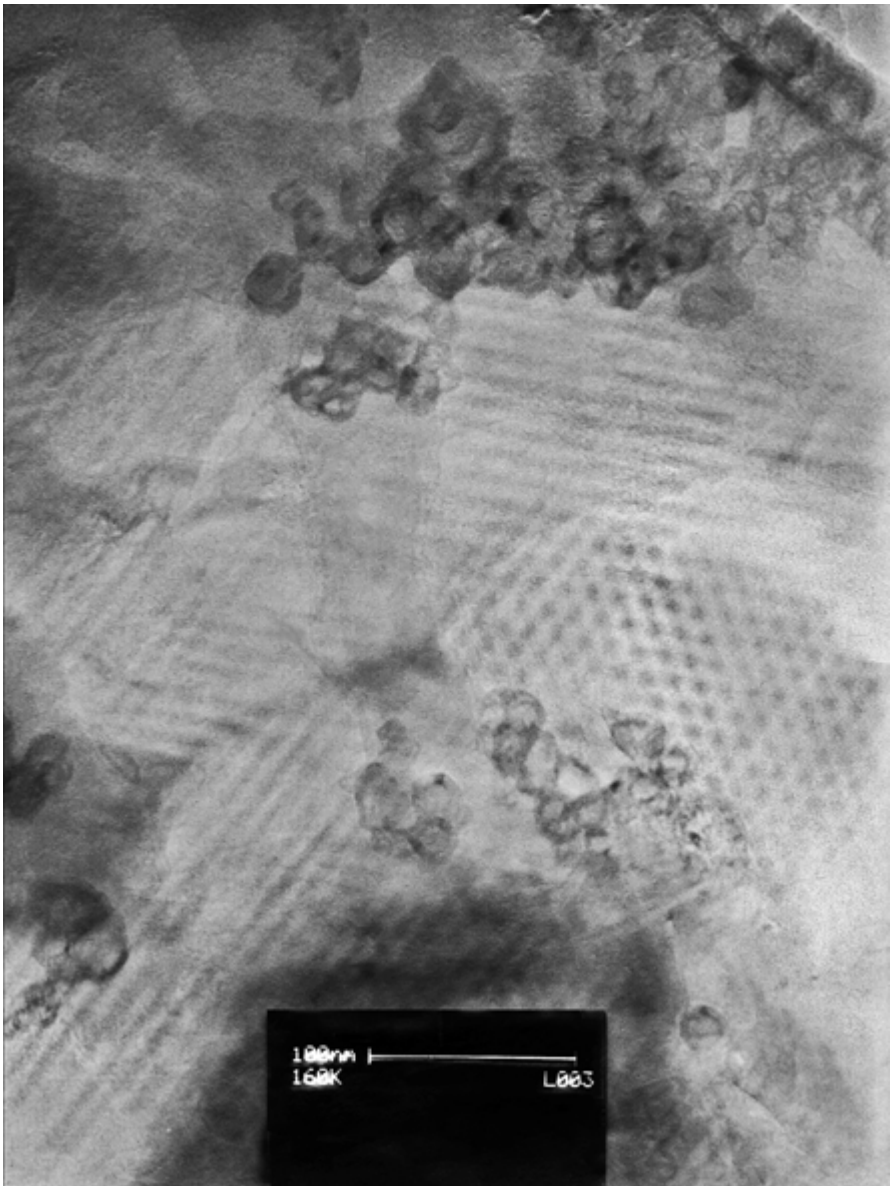
Fig. S2. SEM images of **1** (a-g).



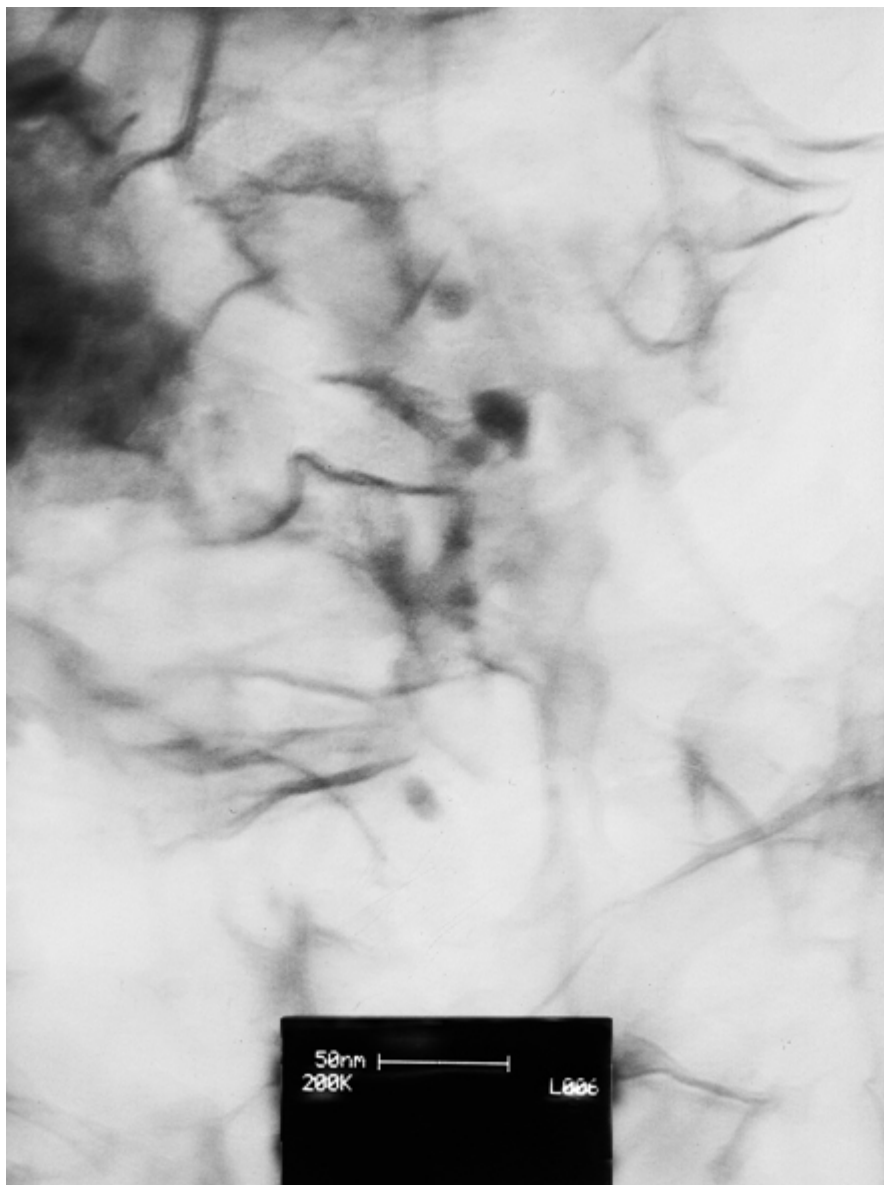
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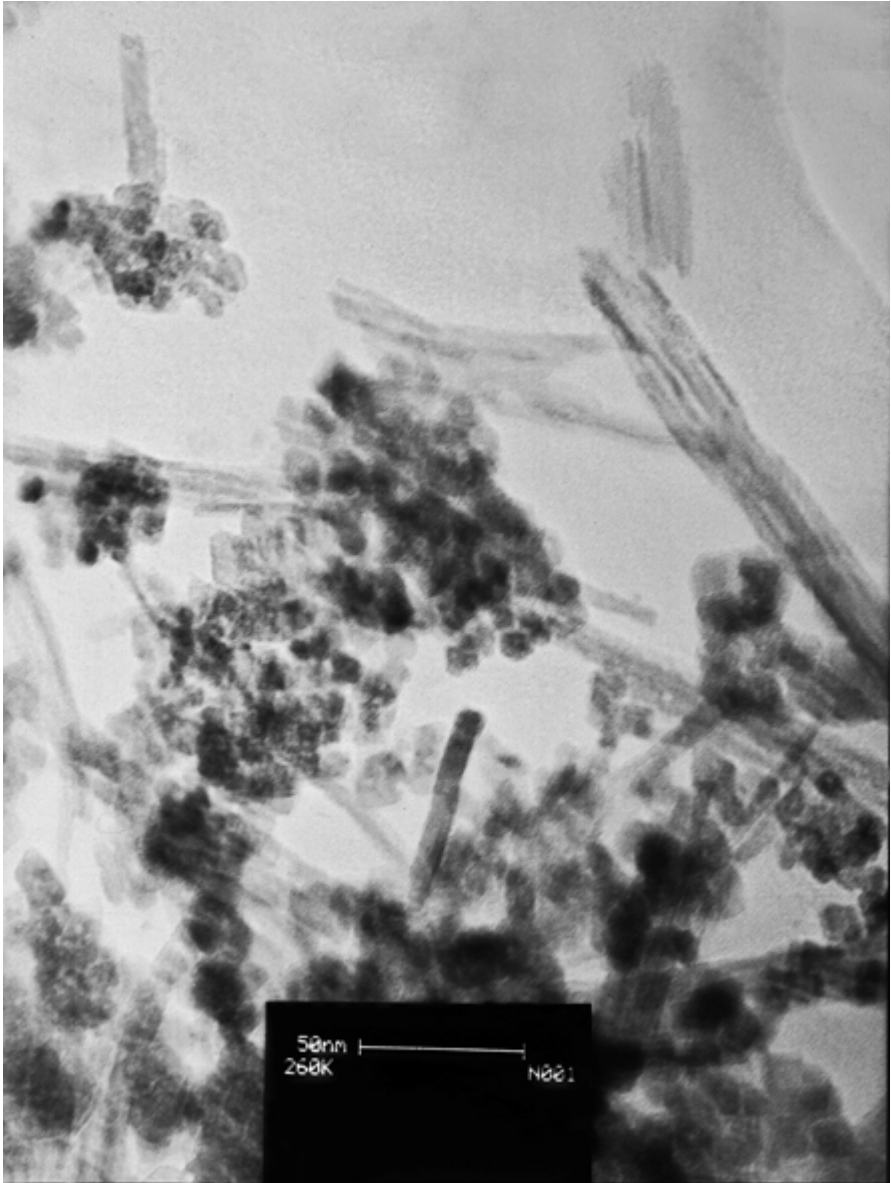
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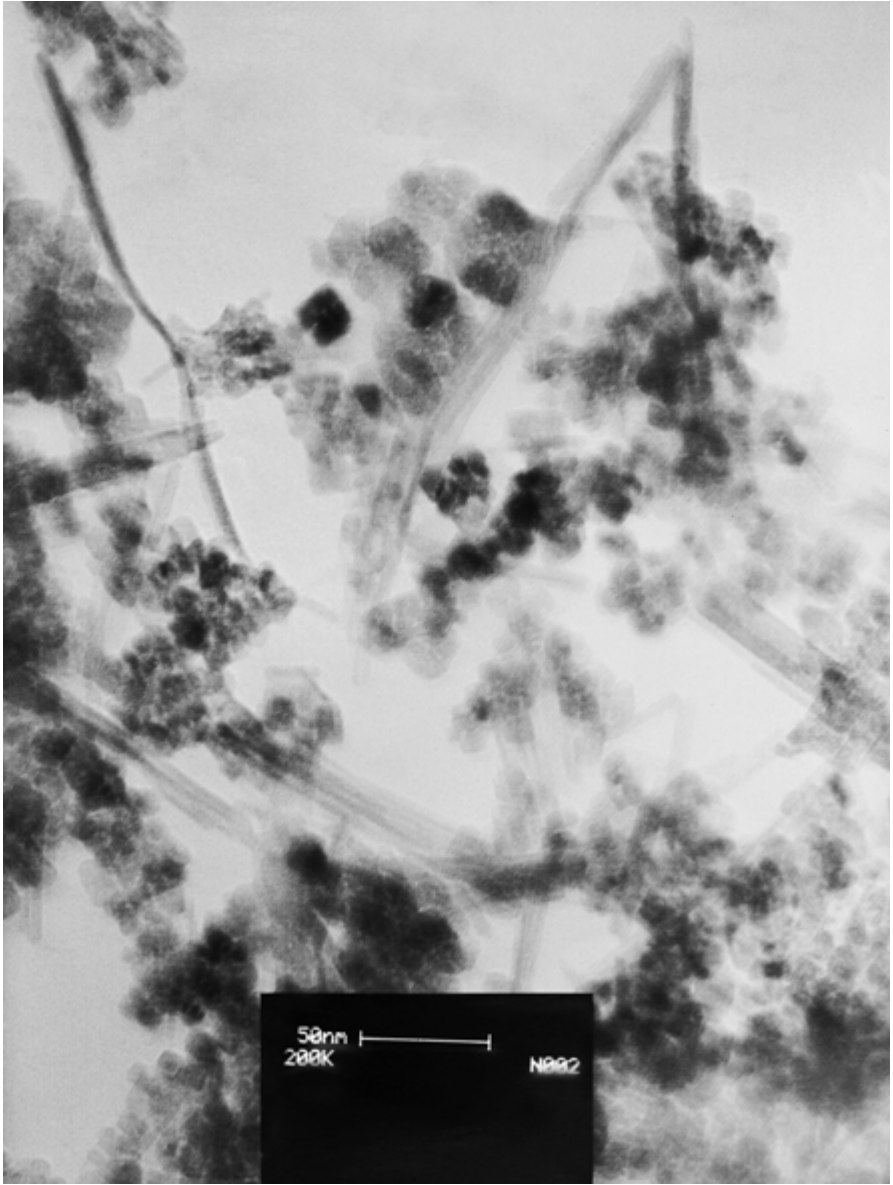
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d
Fig. S3. TEM images of colloidal Birnessite monosheets (a-d).



a



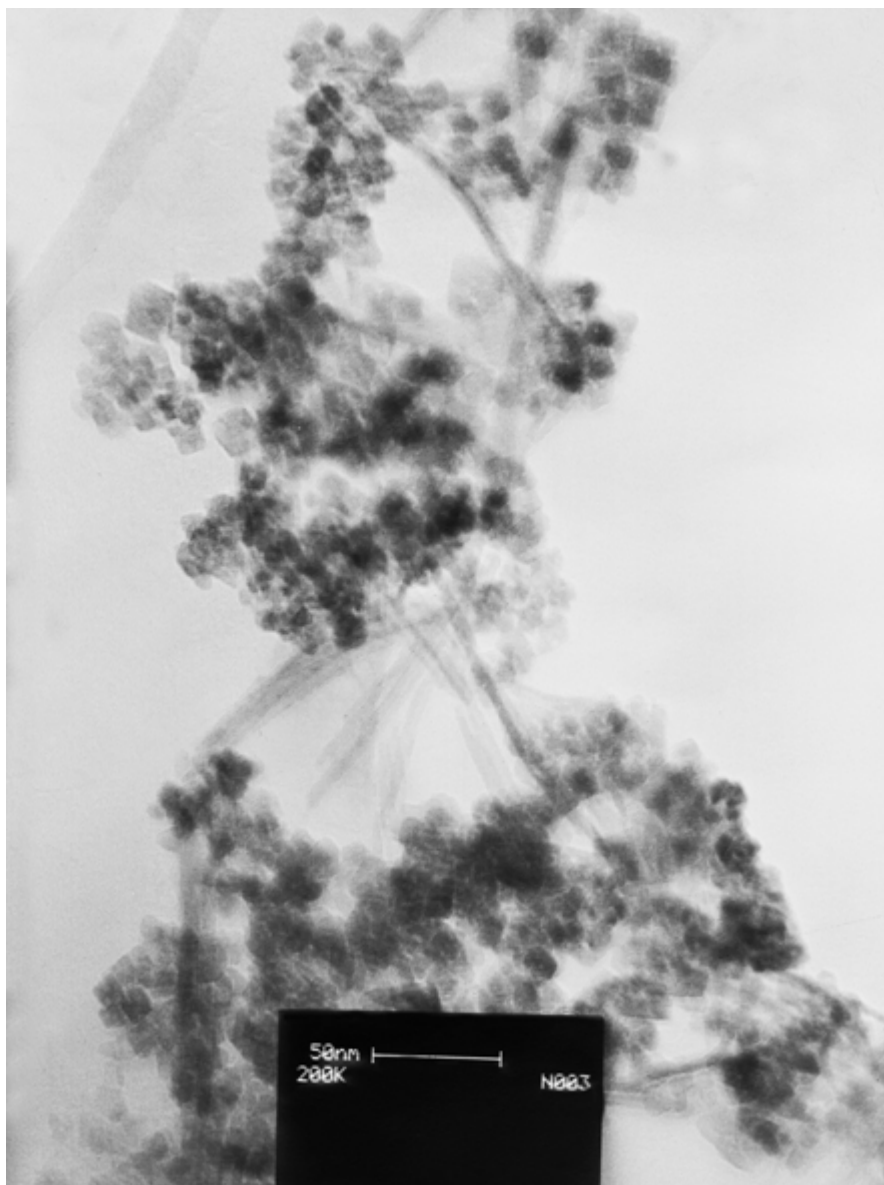
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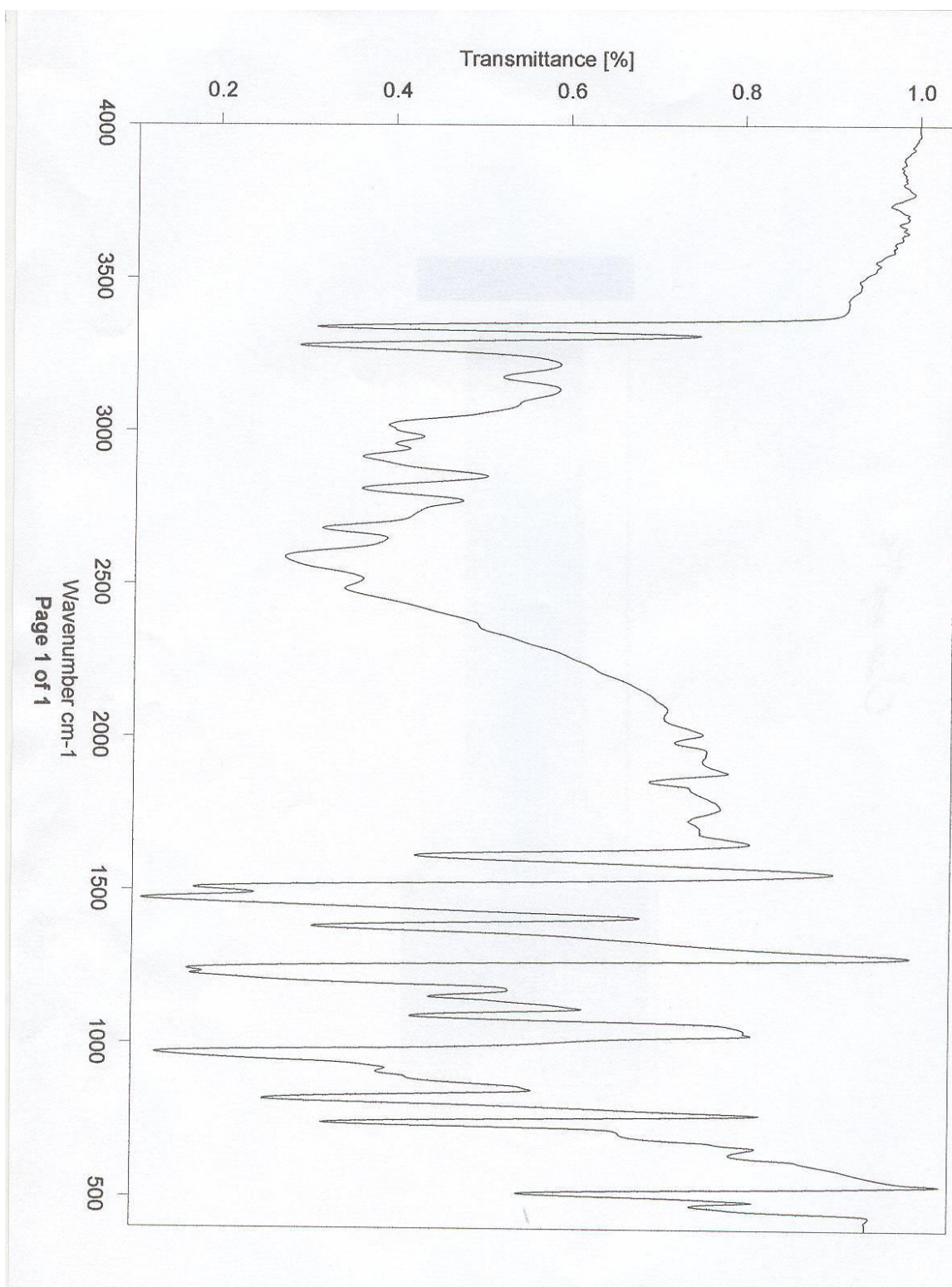


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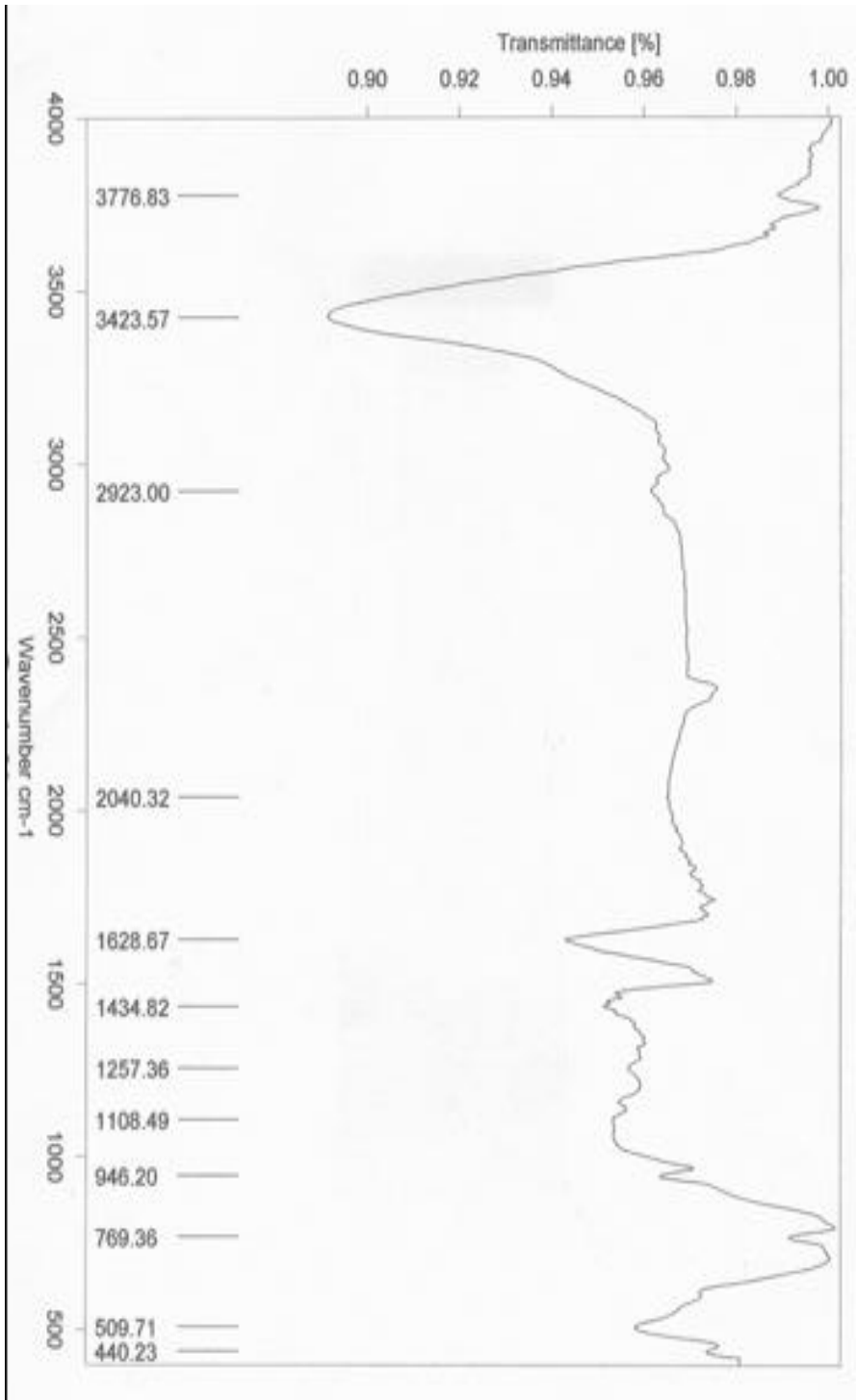


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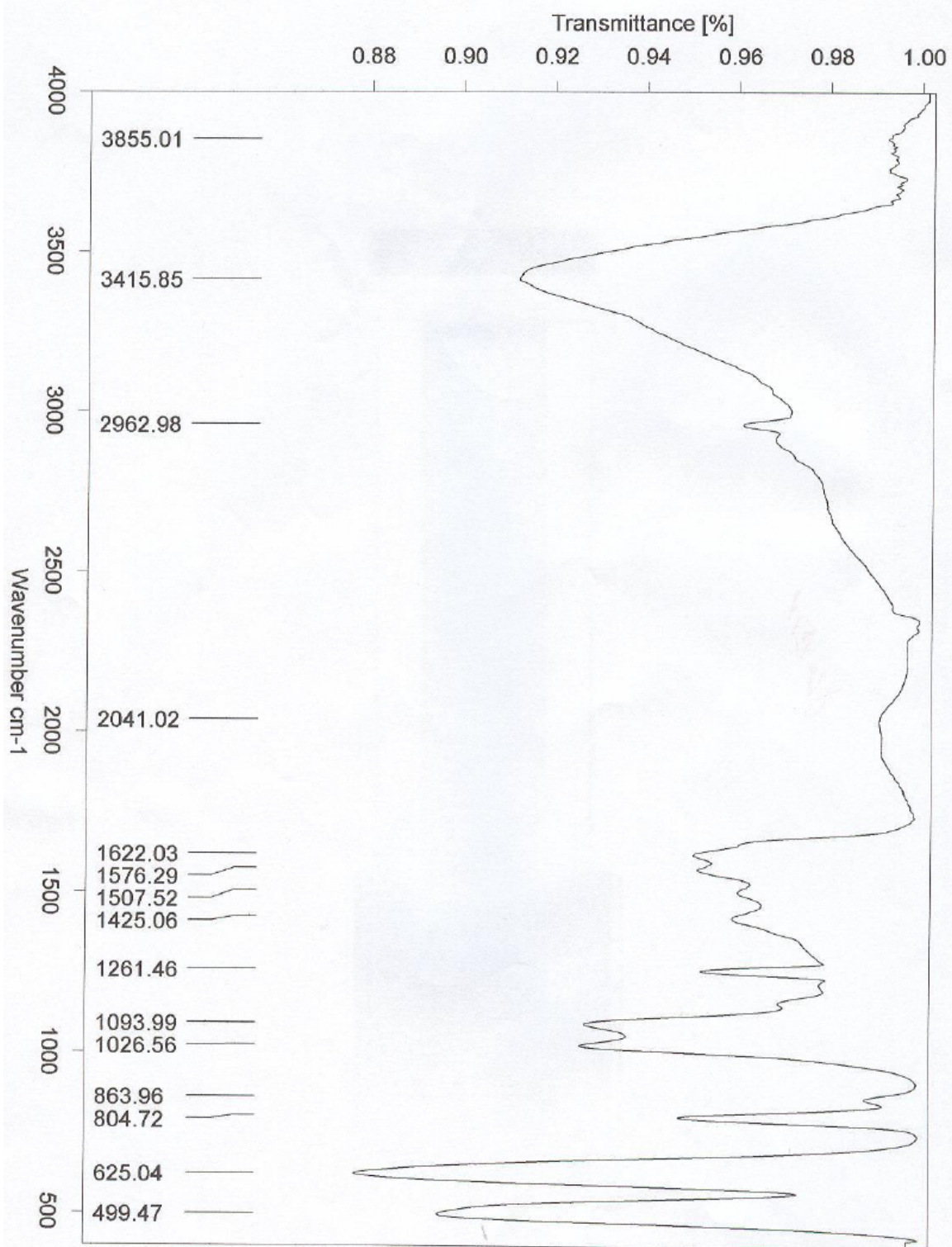
Fig. S4. TEM images of **1** (a-e).



a



b



c

Fig. S5. MIR spectra of 4 - aminophenol (a), manganese (III),(IV) oxide monosheet (b), and the self-assembled layered hybrid of phenol - manganese oxide (c). IR spectrum of **1** indicates the presence of both manganese oxide and 4 - aminophenol in the structure.

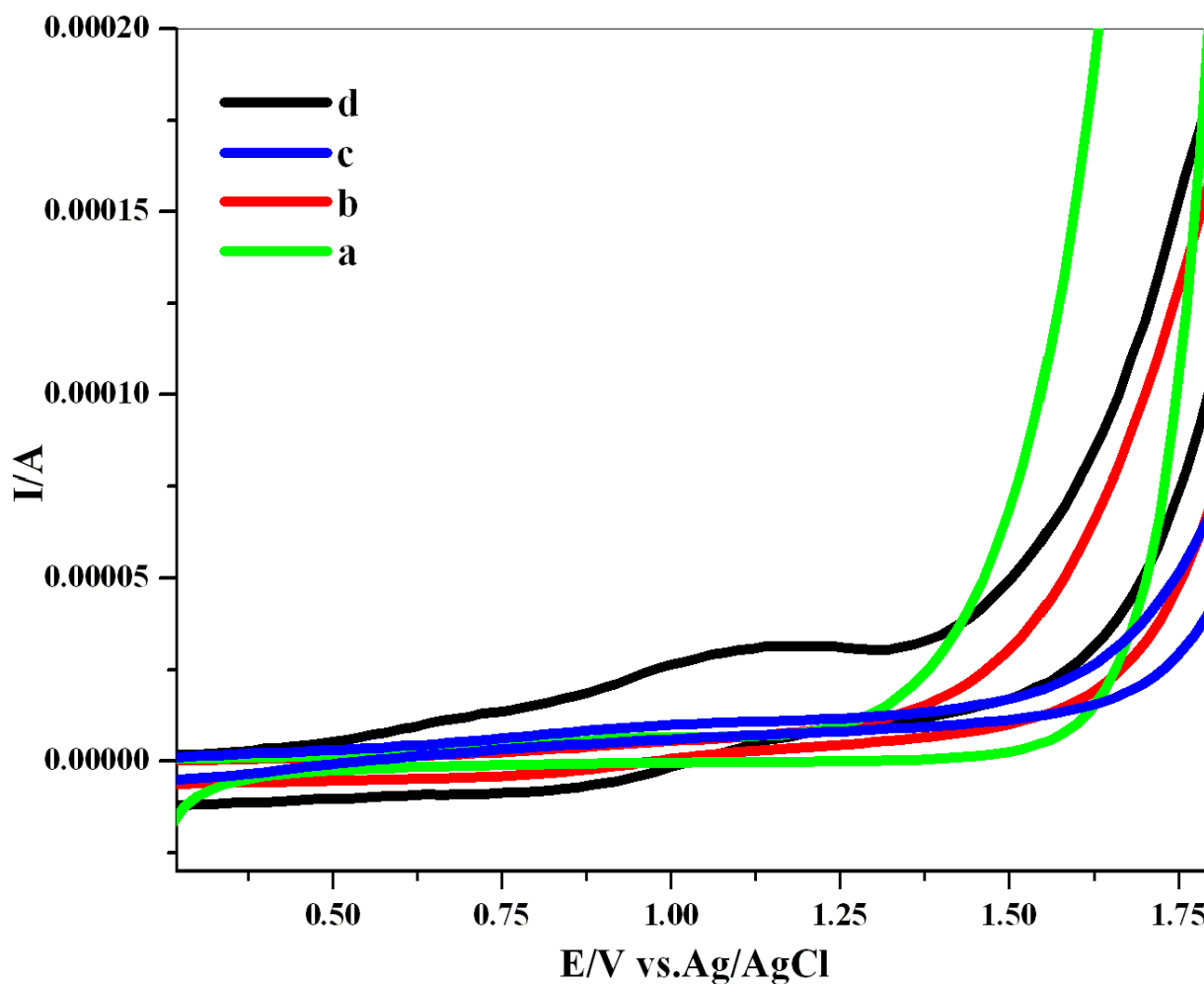


Fig. S6. Cyclic voltammograms of a Pt electrode (a), Pt electrode modified with dried manganese (III, IV) oxide monosheets (b), the Nafion immobilized 4 - aminophenol compound at a Pt electrode (c) and the self-assembled layered hybrid of phenol - manganese oxide (d) in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 50 mV. s⁻¹.

References:

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