Electronic Supplementary Material (ESI) for Chemical Communications

Self-assembled layered hybrid $Ru(bpy)_3^{+2}$/Manganese (III, IV) oxide: A new and efficient strategy for water oxidation

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Materials and 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}. TEM and SEM were carried out with Philips CM120 and LEO 1430VP, respectively. 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. Prior to analysis, the oxide (10.0 mg metal) were added to 1 mL of concentrated nitric acid and H_2O_2, 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 glassy carbon or glassy carbon modified electrode with dried manganese (III, IV) oxide monosheets and an $Ag|AgCl|KCl_{sat}$ served as the working and reference, respectively. The working potential was applied in the standard way using the potentiostat and the output signal was acquired by Autolab Nova software. X-Ray absorption spectroscopy at the K-edges of manganese were performed at the KMC1 beamline at the BESSY synchrotron (Helmholtz-Zentrum Berlin, Germany) at 20 K in a liquid-helium cryostat.

Oxygen evolution studies were carried out with a luminescent DO probe oxygen electrode (HQ40d portable dissolved oxygen meter from Hach company). All solutions were prepared using doubly deionized water. All rates were measured at reported temperature using the method of initial rates from at least 100 s. The temperature of the reactor (a colourless three-neck, round-bottom glass flask (50 ml)) remained constant with a bath and a constant stirring rate was also maintained.

Preparation of Colloidal Birnessite Monosheets[1]:

20.0 mL of a mixed aqueous solution of TMA·OH (0.6 M) and 3.0 wt % 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 RT. 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 RT.

Preparation of Self-Assembled Organic-Inorganic Layered Hybrid $Ru(bpy)_3/MnO_2$:

0.25 g (0.33 mmol) of $Ru(bpy)_3Cl_2$ was dissolved in 10 mL water and the solution was added to 50 mL of the colloidal suspension of MnO_2 monosheets (4 mM) during N_2 bubbling at RT and in dark condition. After a few minutes of stirring, flocculation occurred in the mixed solution. The resulting brown precipitate was filtered off, washed water and air-dried at RT and in dark condition (yield 70%). The $Ru(bpy)_3$/ MnO_2 ratio was estimated to be 0.068 on the basis of atomic absorption spectroscopy. **1** can be formulated as $(Ru(bpy)_3)_{0.068}MnO_2.2H_2O$. Anal. Calc. for $C_{2.04}H_{5.63}MnN_{0.41}O_4Ru0.068$ Found: C, 14.9; H, 3.64; N, 3.40 requires C, 15.15; H, 3.51; N, 3.53%.

Water Oxidation Experiment

Photochemical water oxidation experiments were conducted in a colourless three-neck, round-bottom glass flask (50 ml) containing 40.0 ml of aqueous buffer (acetate and acetic acid, 0.05 M) with pH held at 4.5, $[Co(NH_3)_5Cl]Cl_2$ (10.0 mM), and **1** (26.0 mg). One neck of the flask was closed by a septum (rubber stopper) after deaeration with argon whilst the sensor of the oxygen meter (HQ40d) was introduced into the solution through the other neck of the flask, to measure the amount of oxygen evolved during the irradiation. The third neck was used to introduce an aqueous suspension containing several particles of **1** into the reaction flask. To show that no oxygen entered the reaction flask due to an air leak, the reactor was maintained in the dark for 10 min prior to irradiation while oxygen levels in the flask were monitored. The irradiation of the aqueous reaction mixtures containing **1** was carried out while the reaction flask (reactor) was maintained in a metacrylate thermostatted water bath at 25.0 ºC. The irradiation was with visible light ($\lambda > 400$ nm) from a 250W tungsten lamp or sunlight. The illumination intensity was ~5,000 lux as determined with a MS-1300A luxmeter. A cut-off light filter (was placed between the light source and the sample in the reactor to ensure that only visible light ($\lambda > 400$ nm) reached the samples.

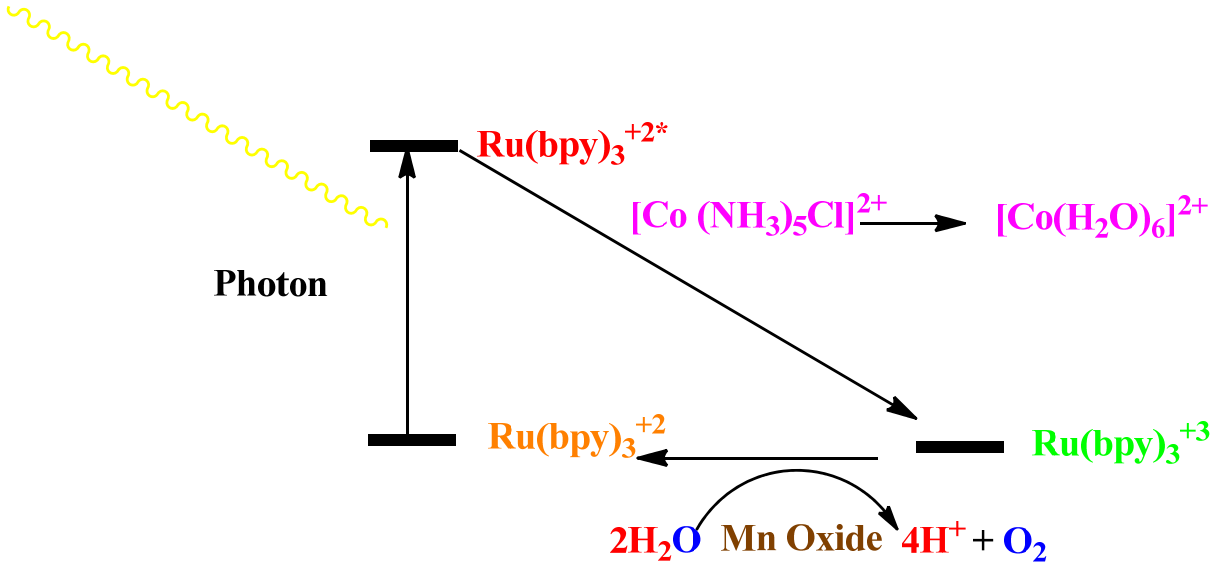

Fig. S1. Schematic of the photocatalytic water oxidation by the $[Ru(bpy)_3]^{2+}$ as a photosensitizer

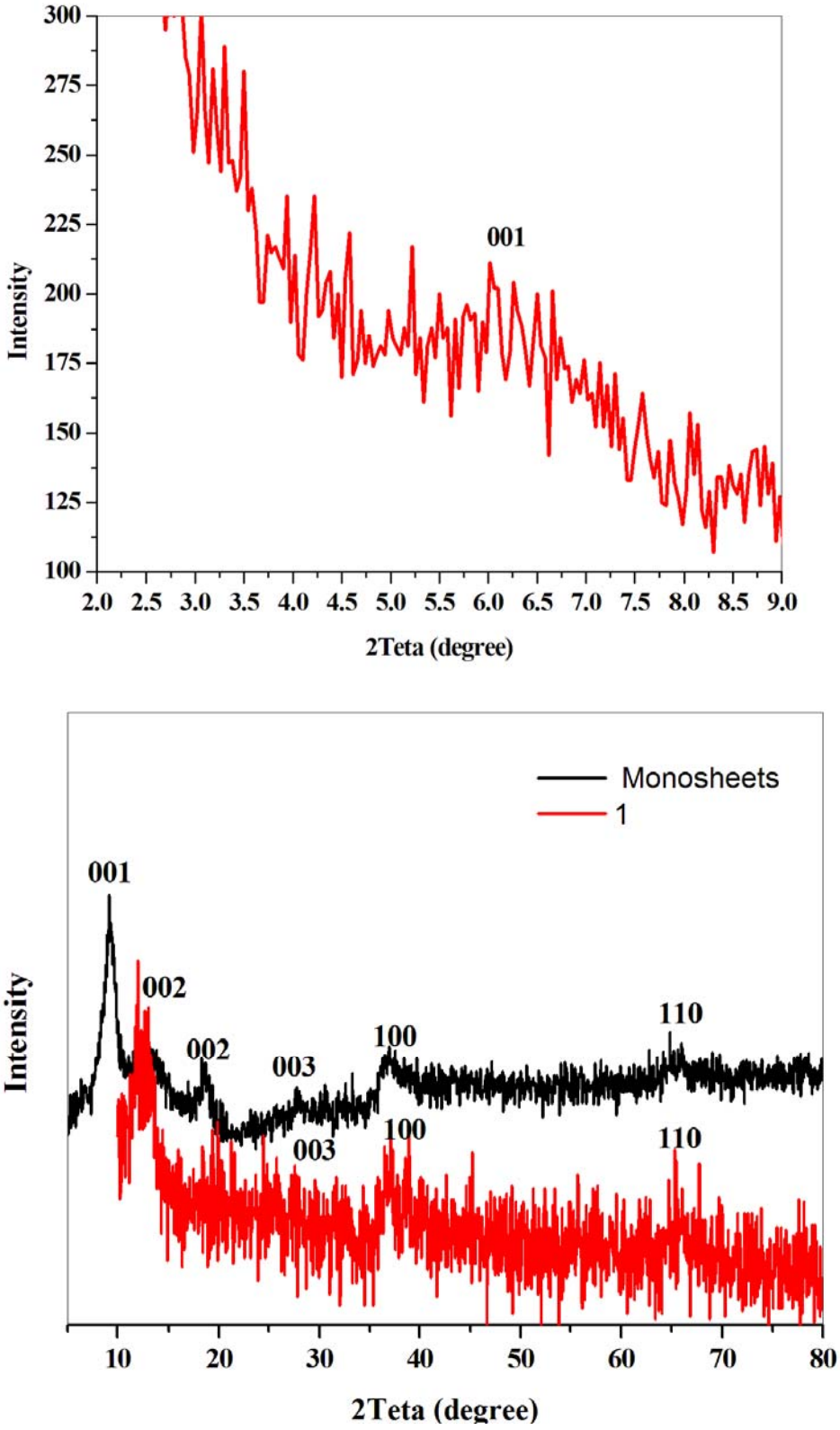

Fig. S2. Powder X-ray diffraction patterns of **1 (**red) and dried manganese (III, IV) oxide monosheet (black).

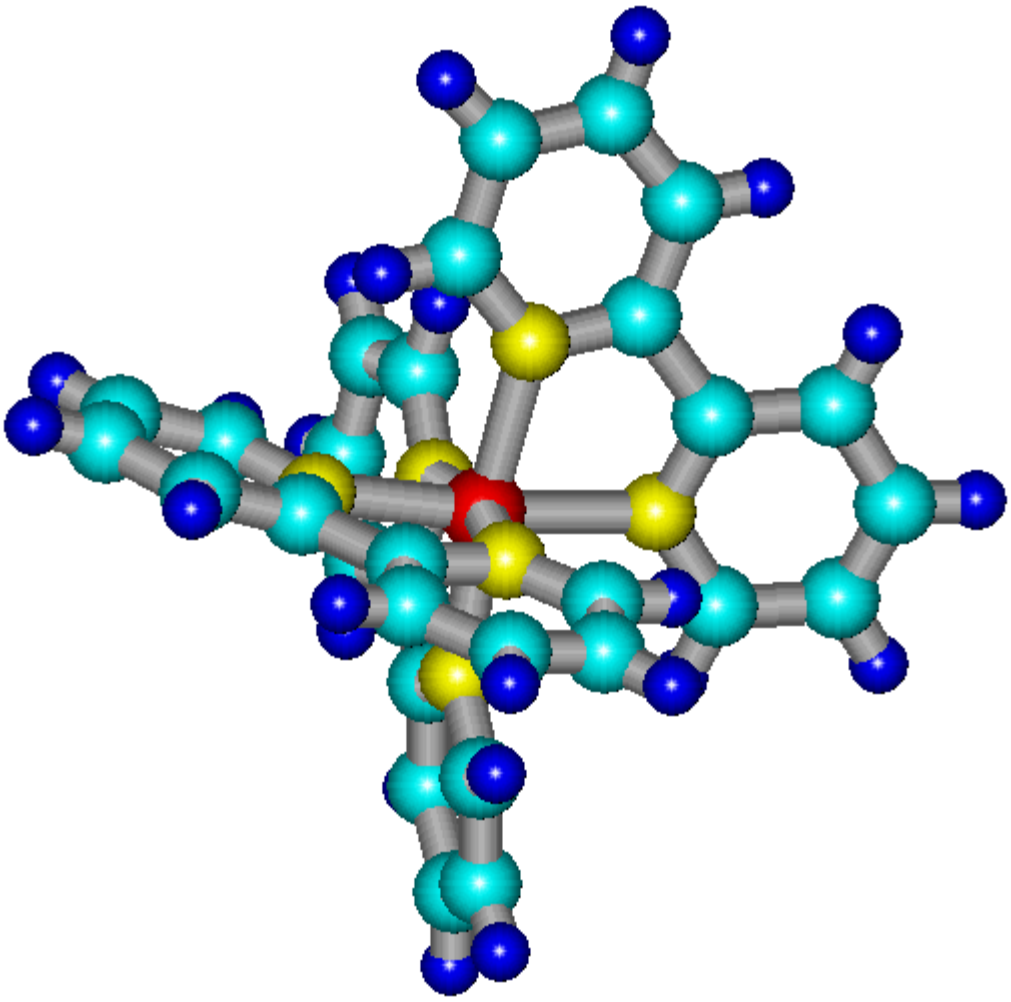

Fig. S3 XRD patterns of a dried sample of **1** indicated that it has a birnessite structure and the interlayer spacing is ~ 1.3 nm related to arrangement of $[Ru(bpy)_3]^{2+}$ between layers. A proposal $[Ru(bpy)_3]^{2+}$ analogues oriented between layers is shown in this figure.

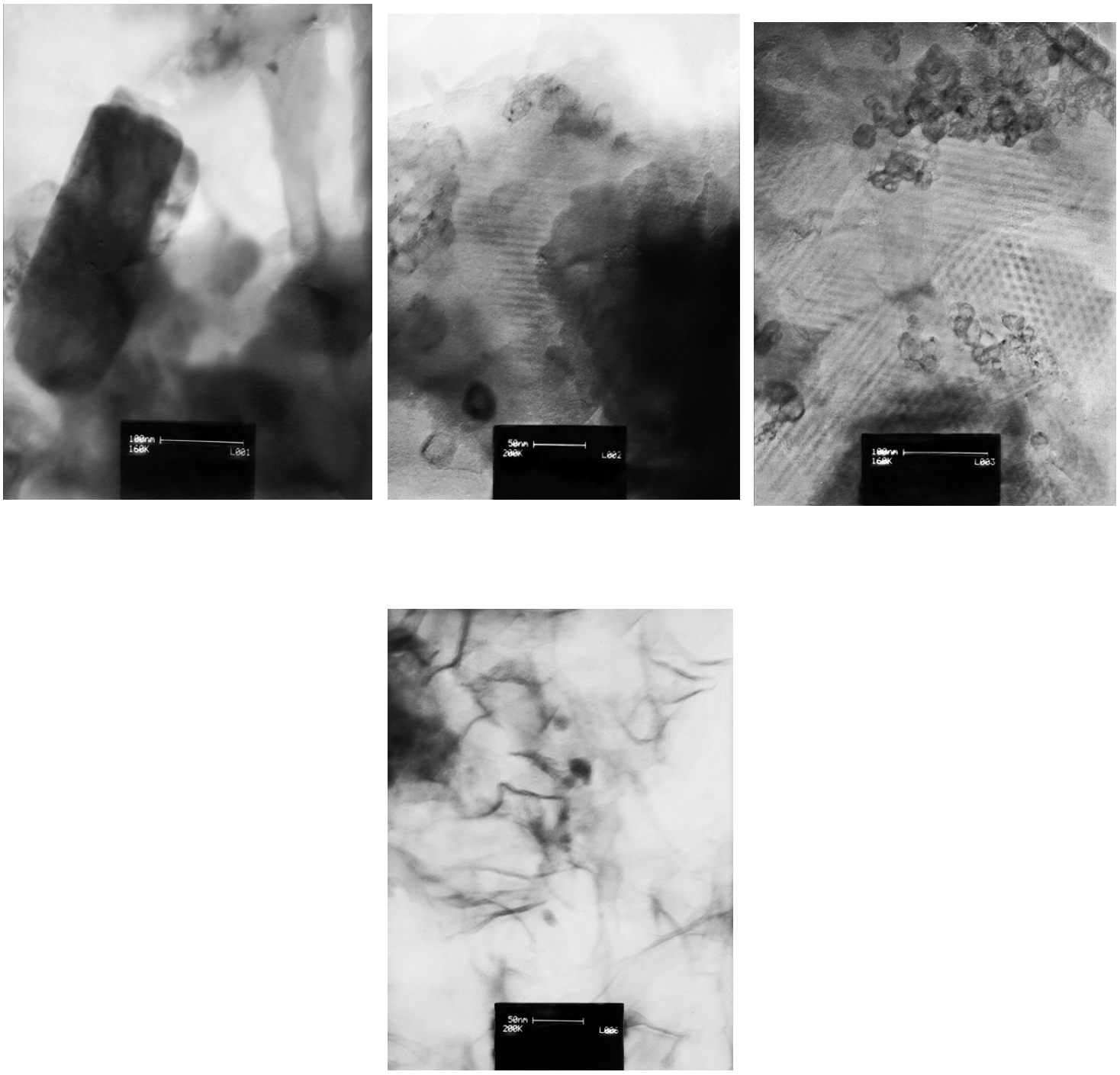

Fig. S4. TEM images of colloidal birnessite monosheets.

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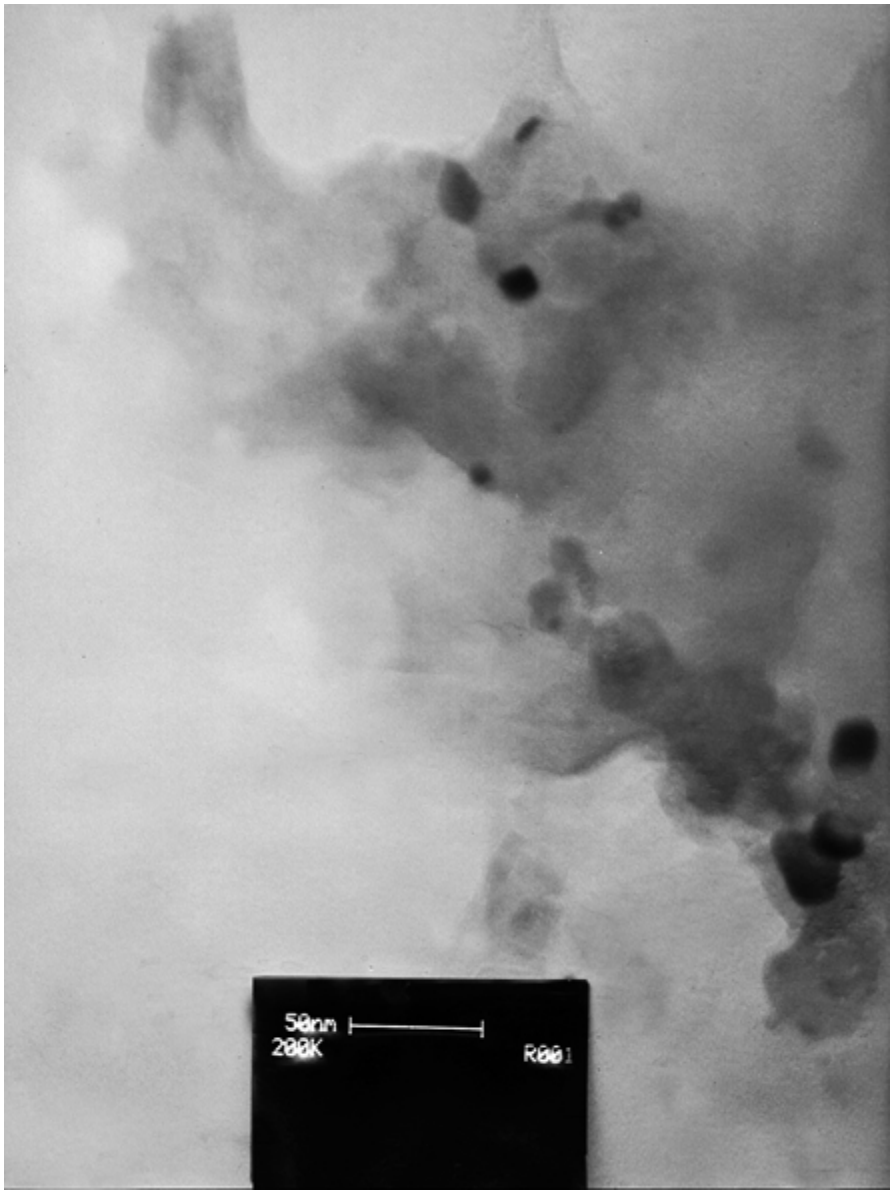
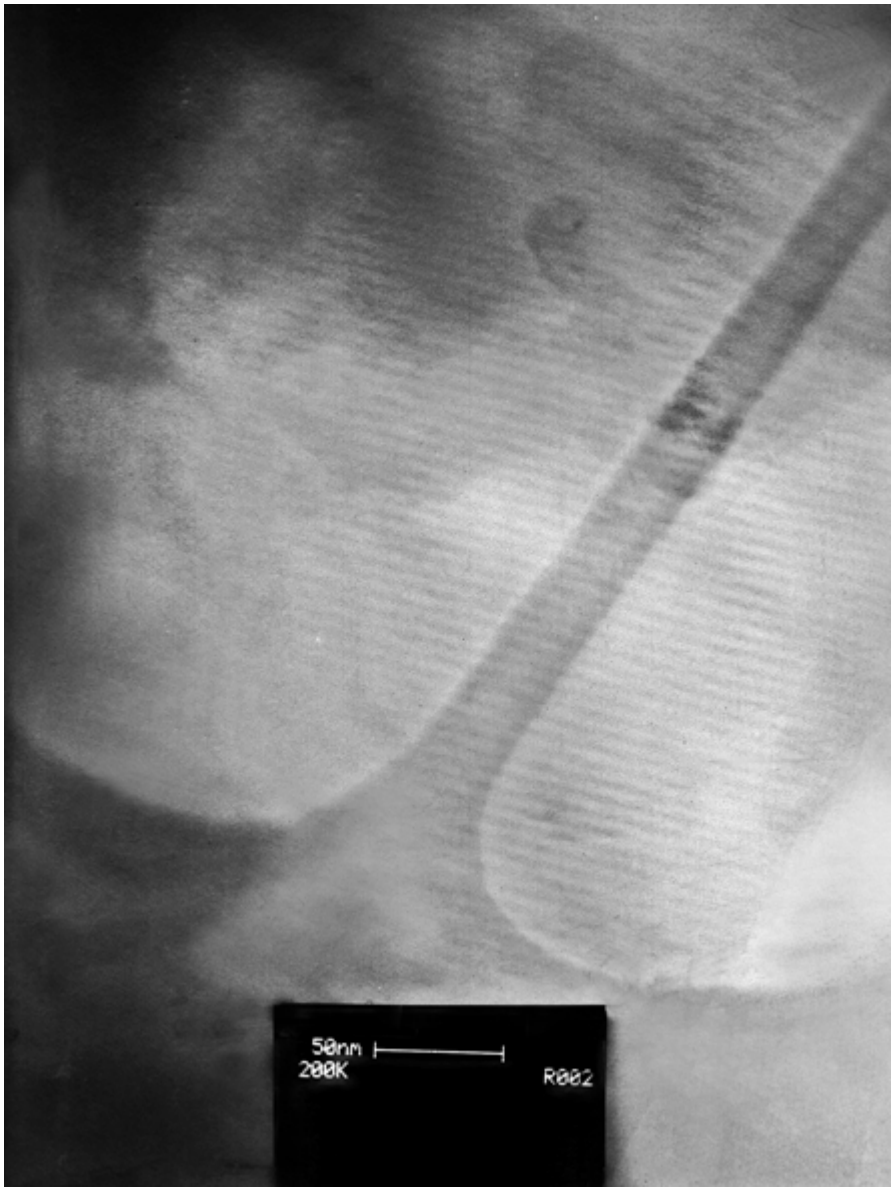




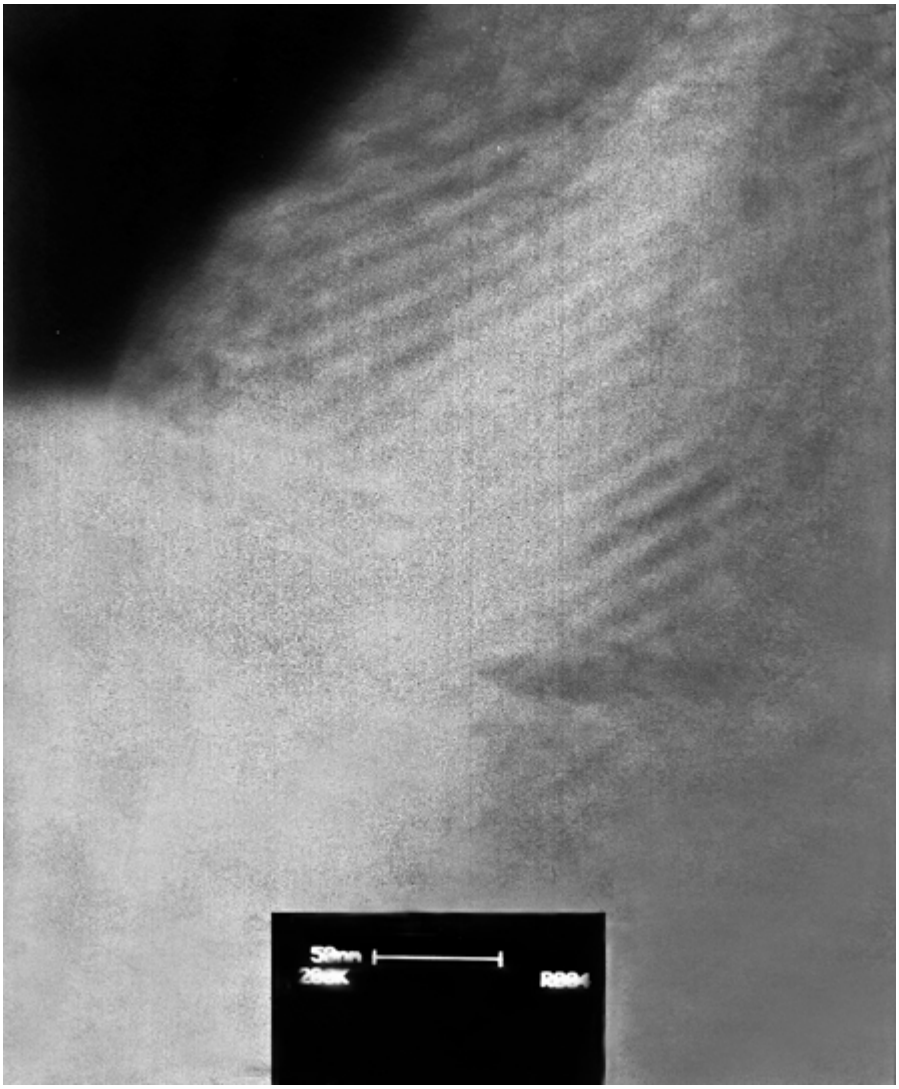
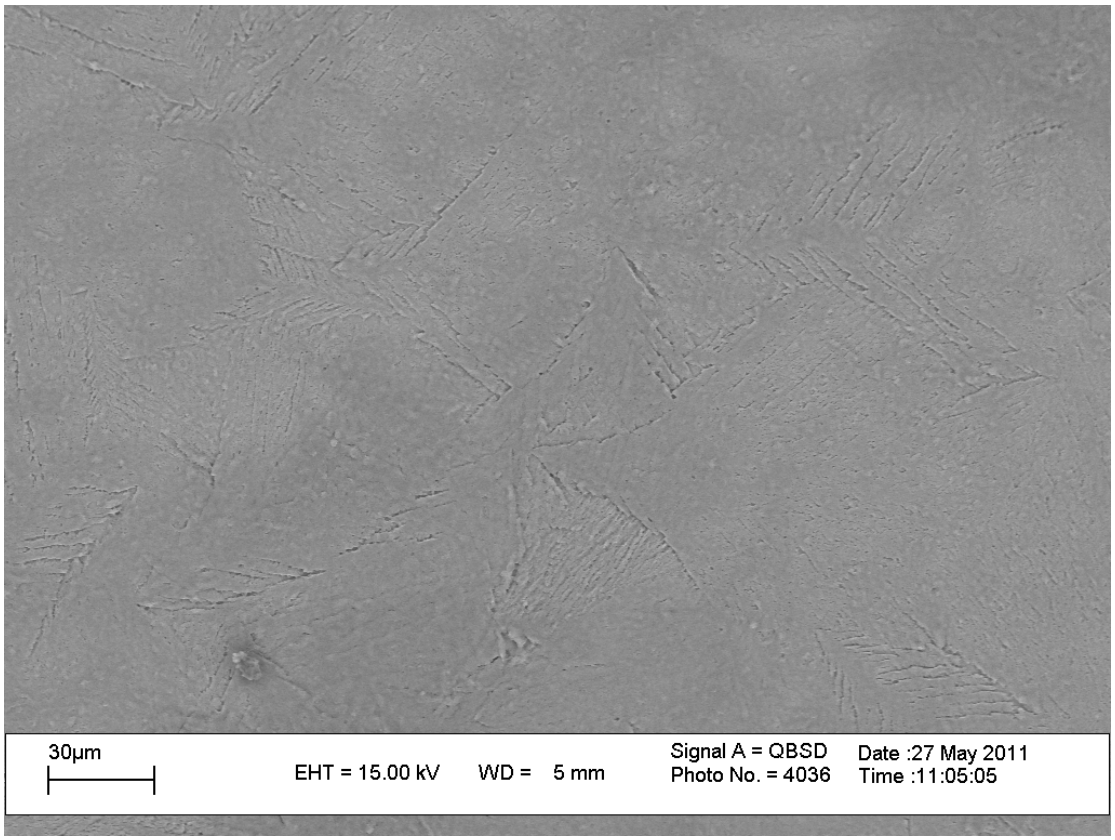
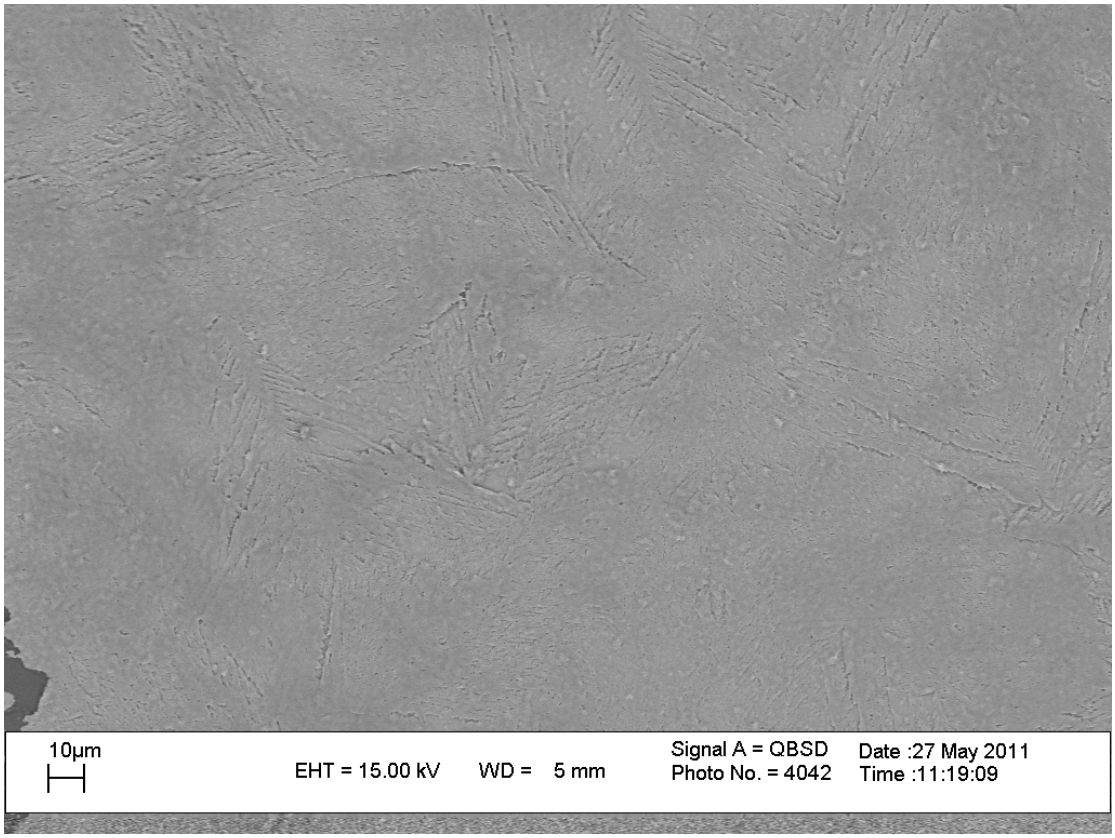
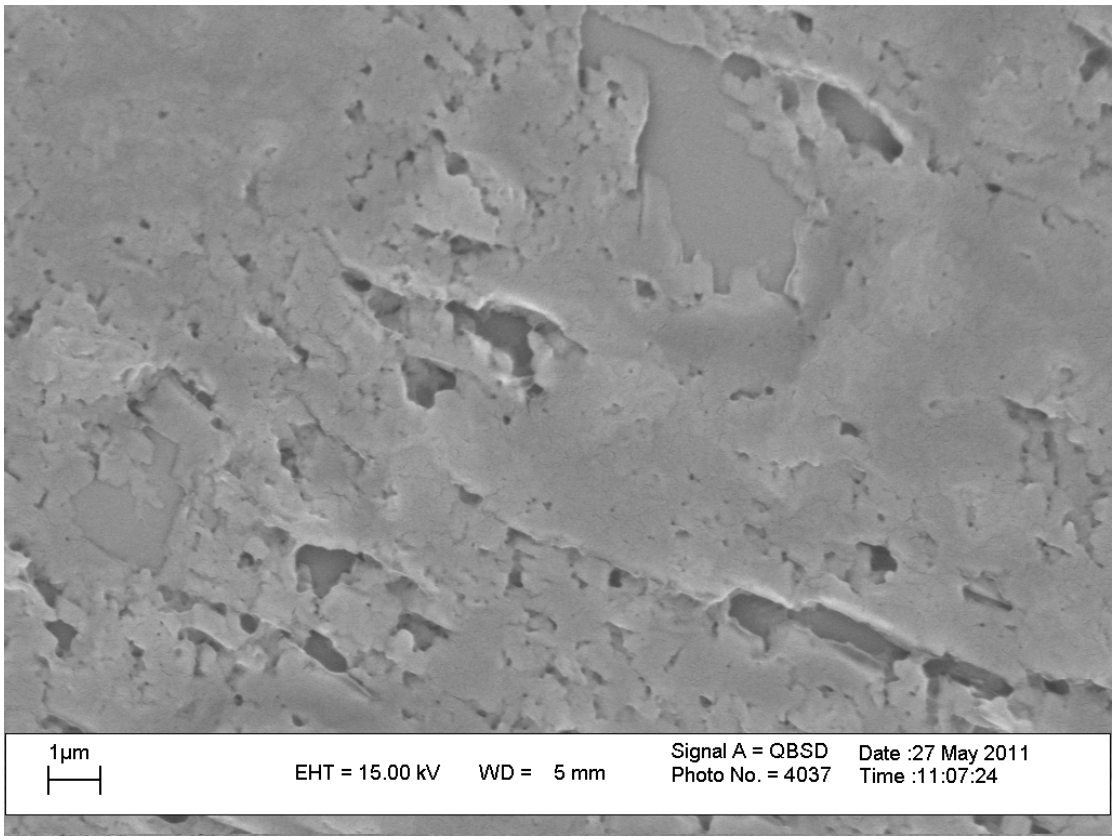
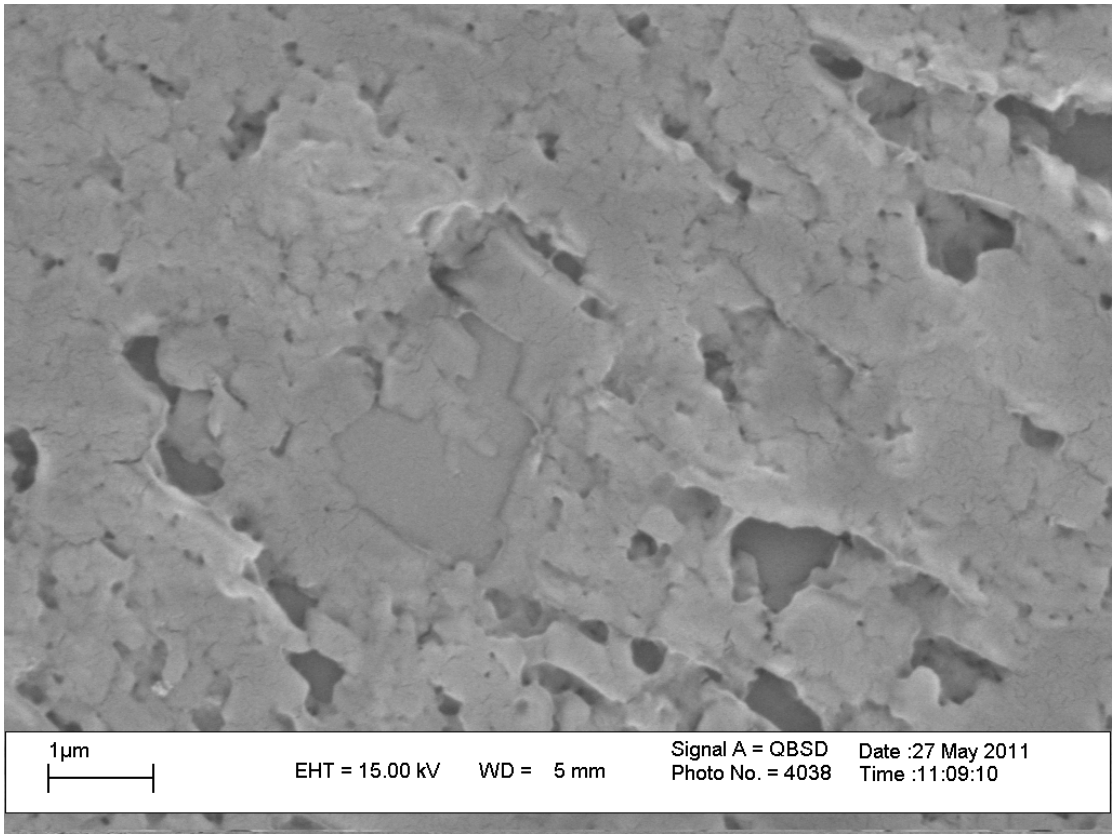


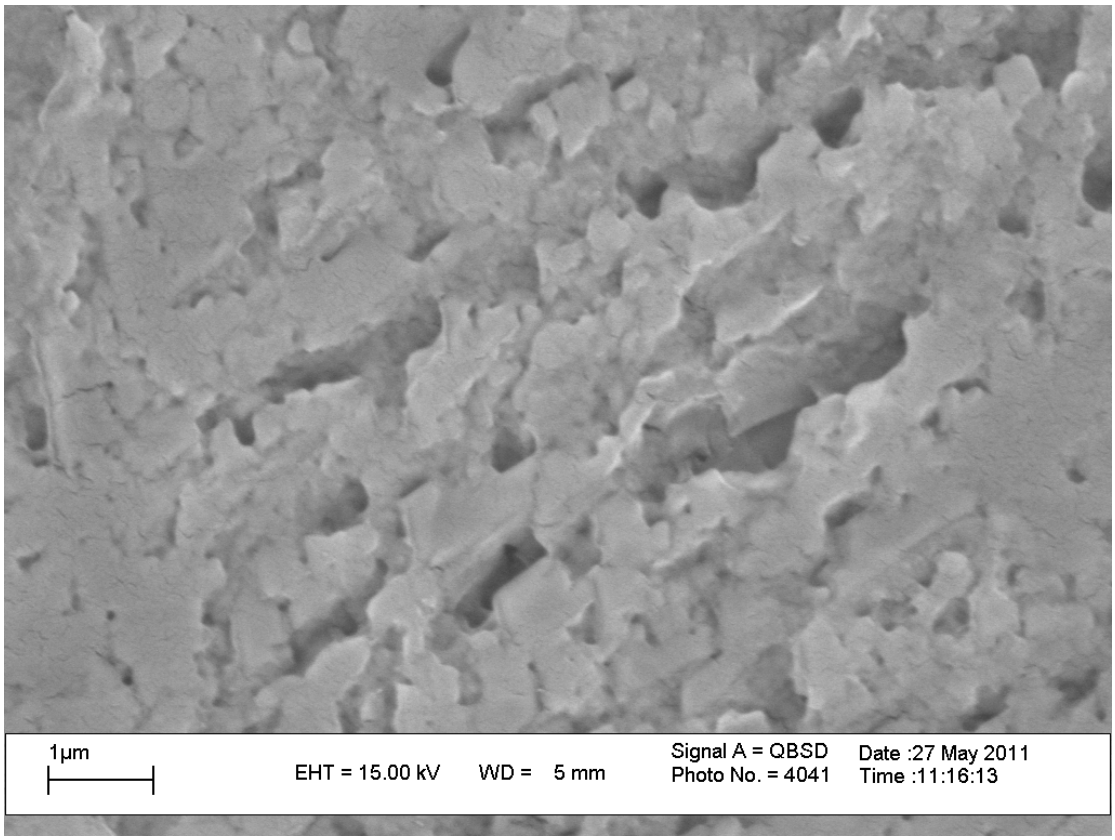
Fig. S5. TEM images of **1**.

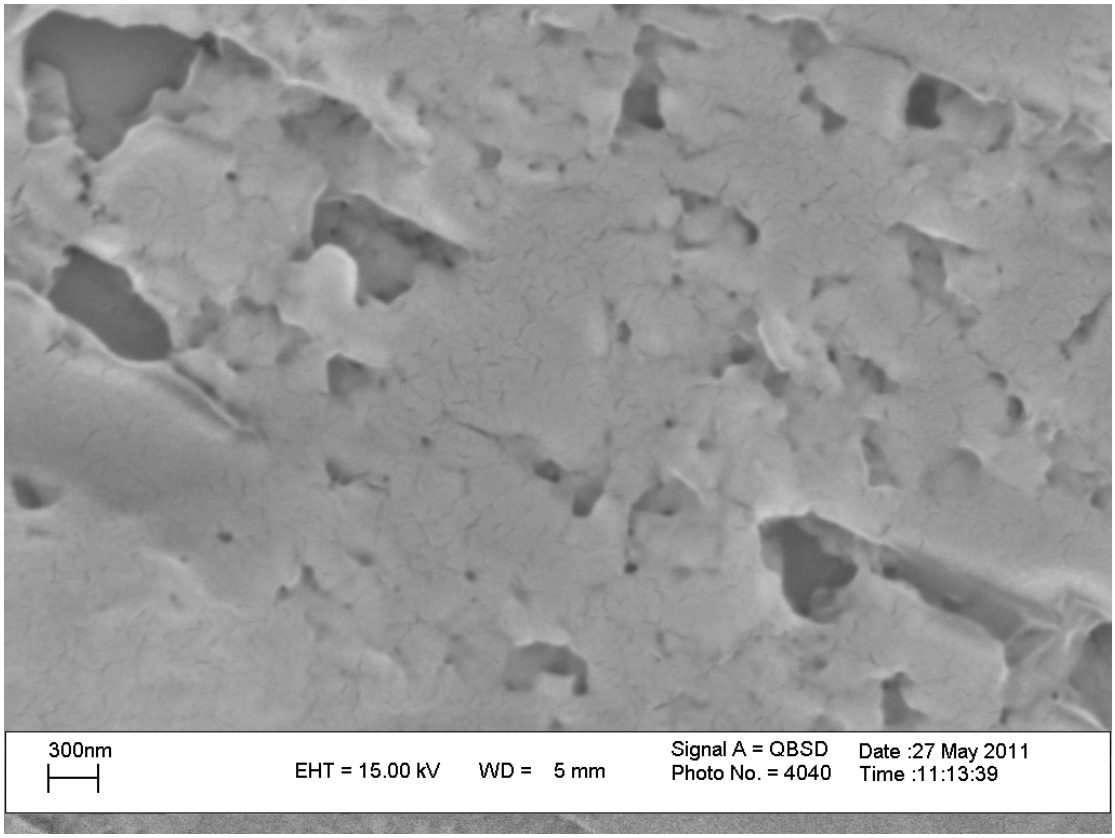












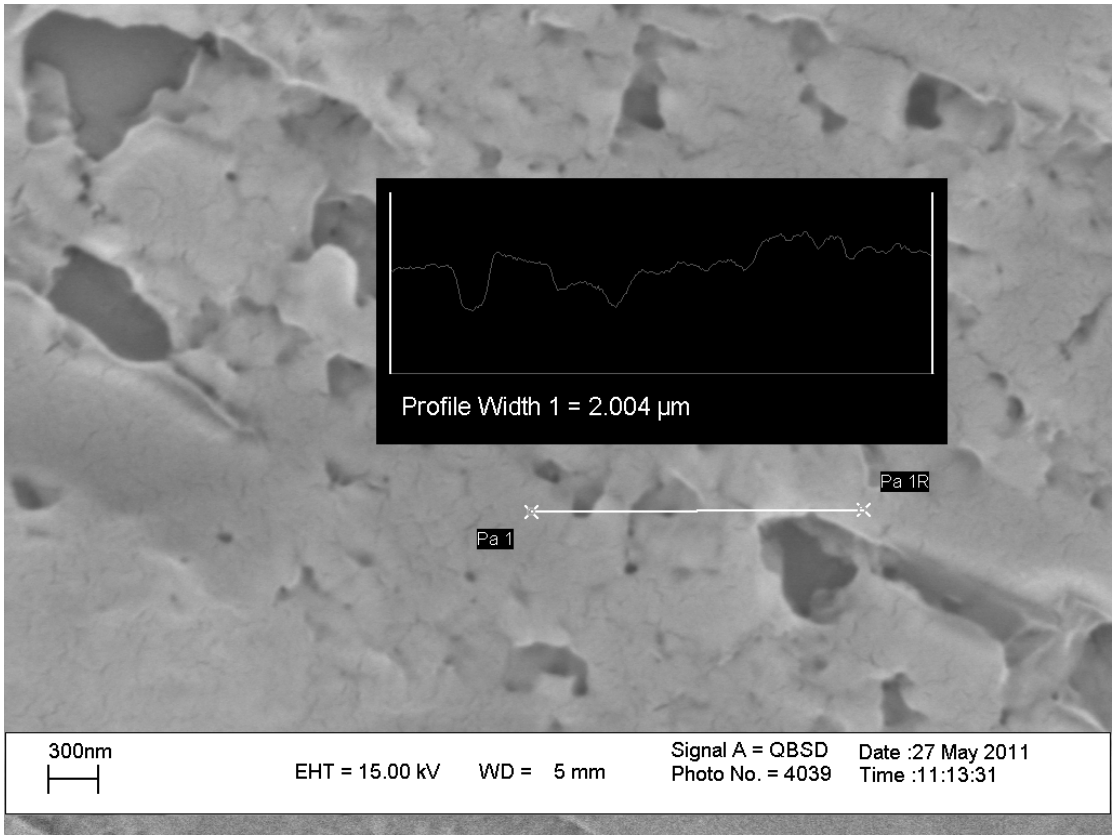
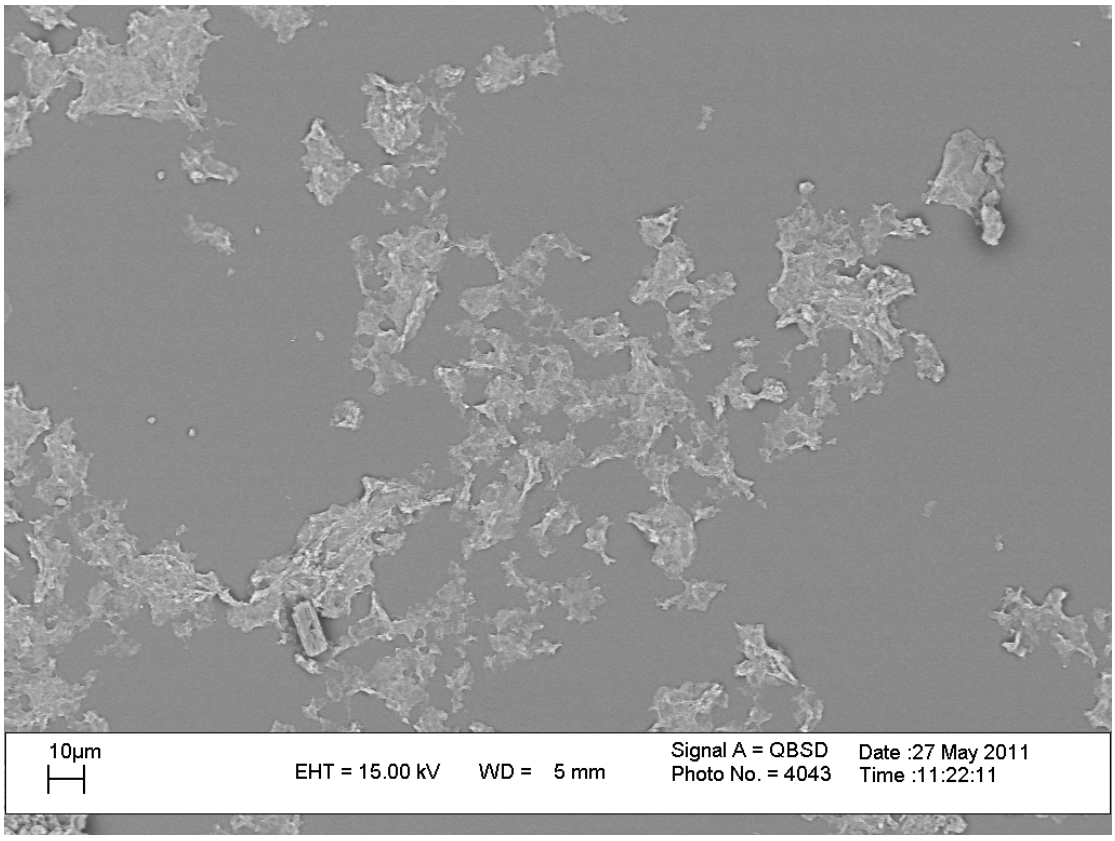
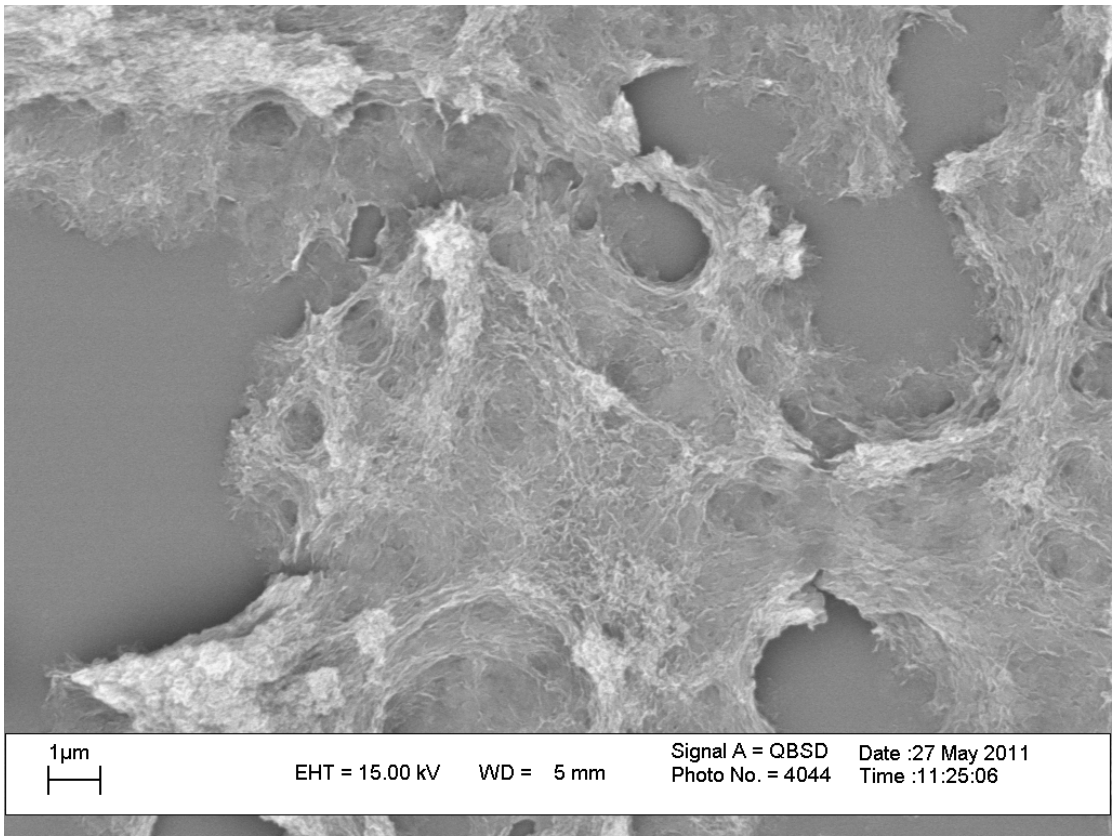
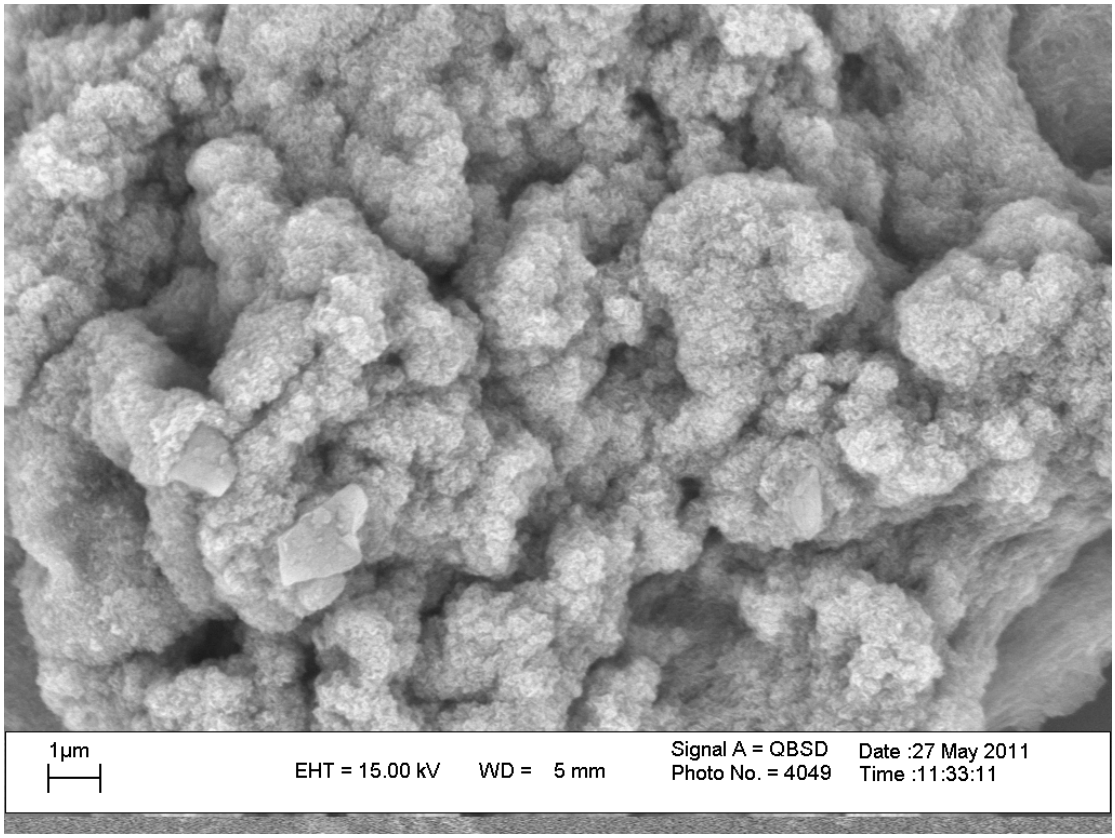
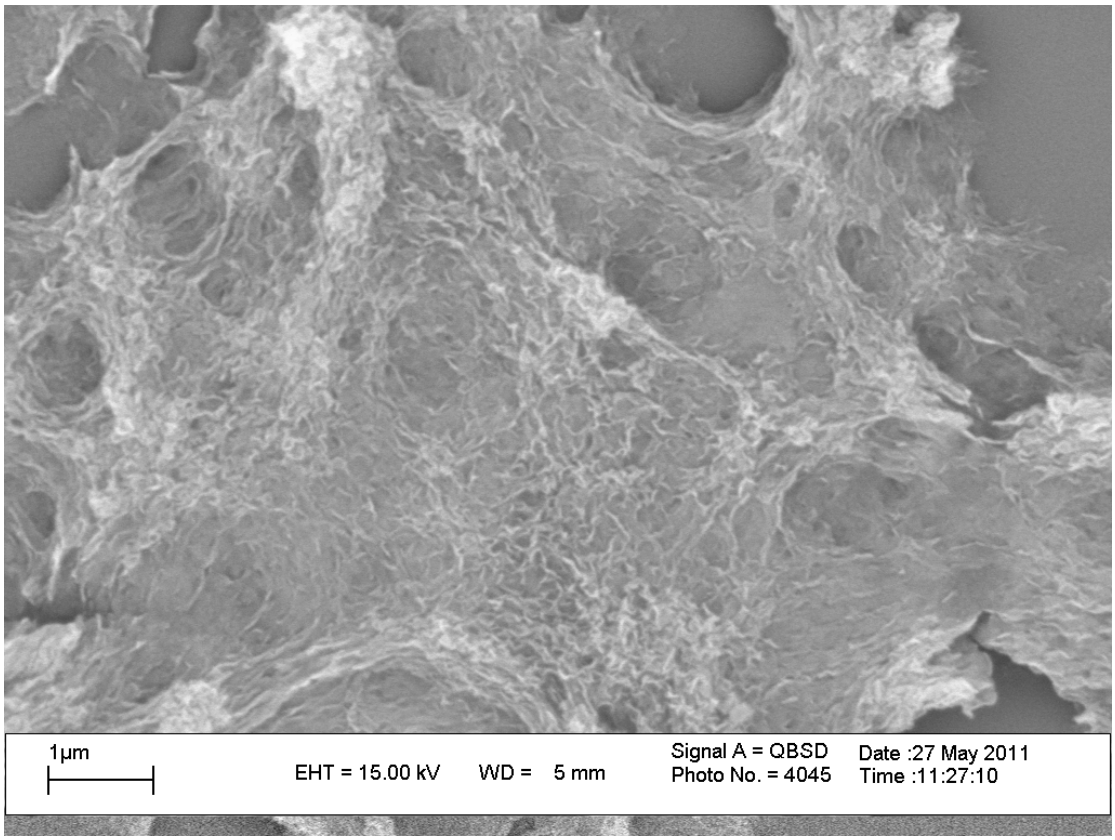


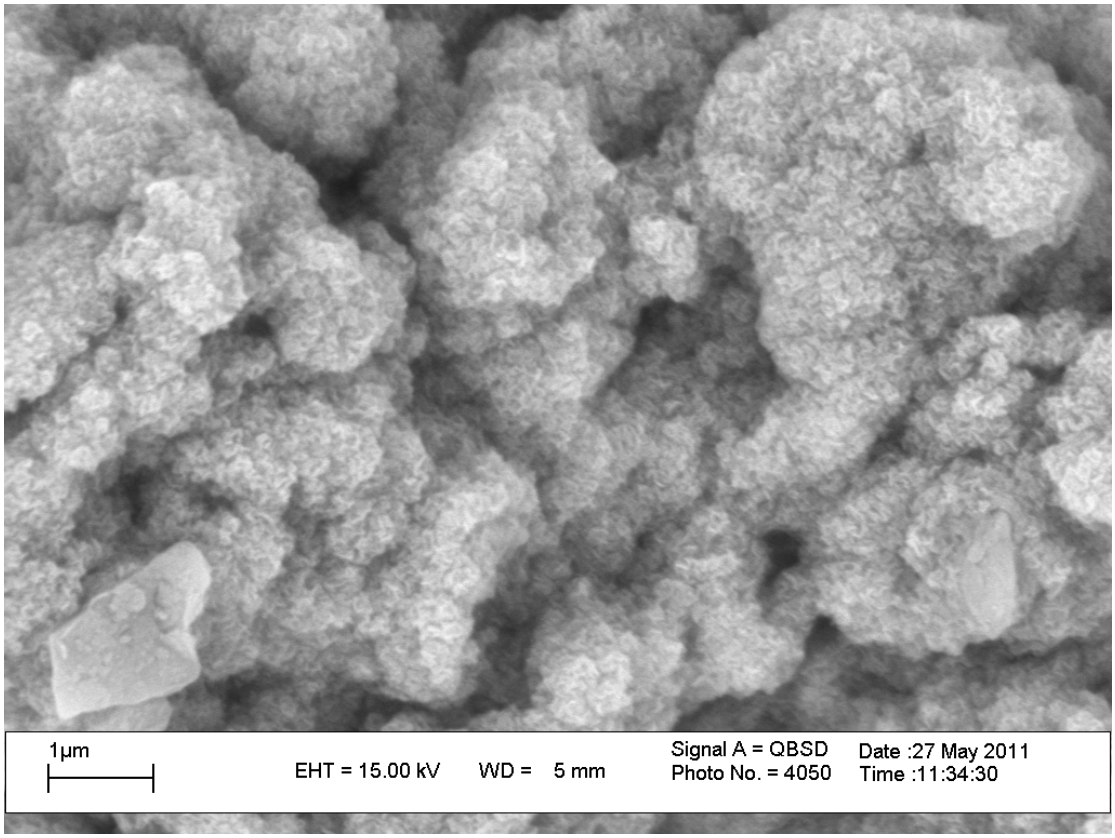
Fig. S6. SEM images of colloidal Birnessite monosheets.

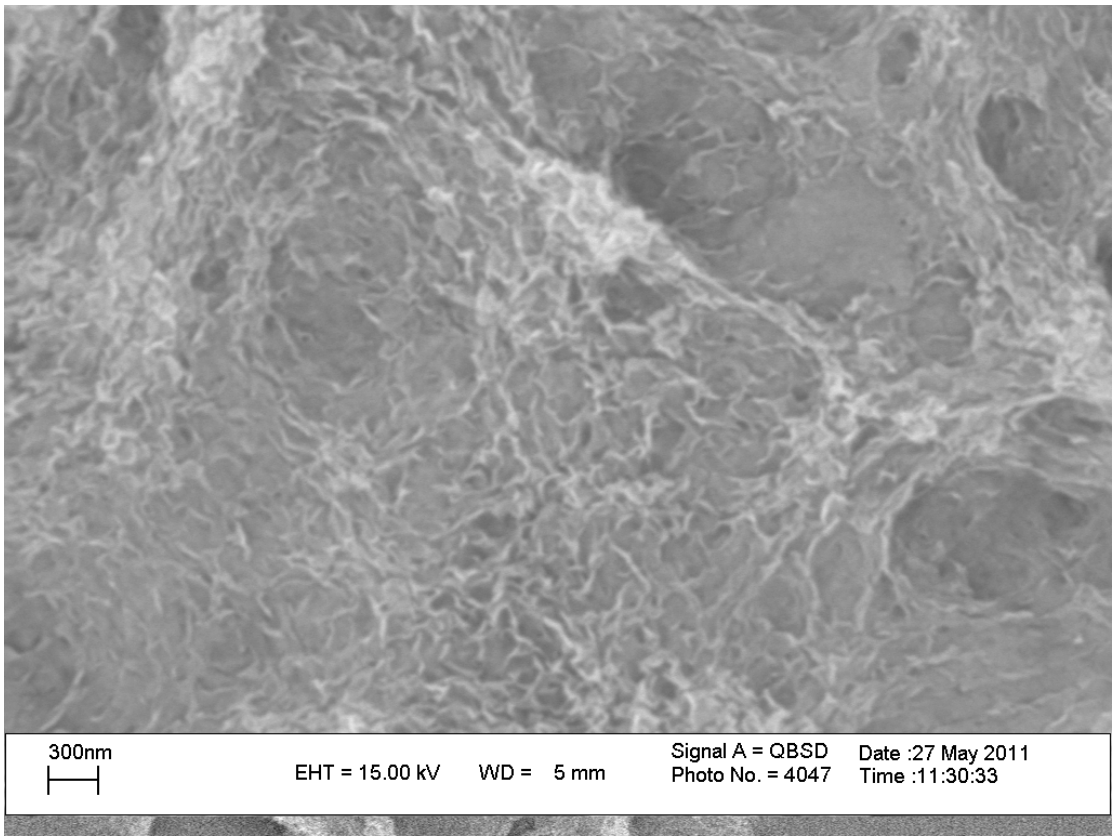


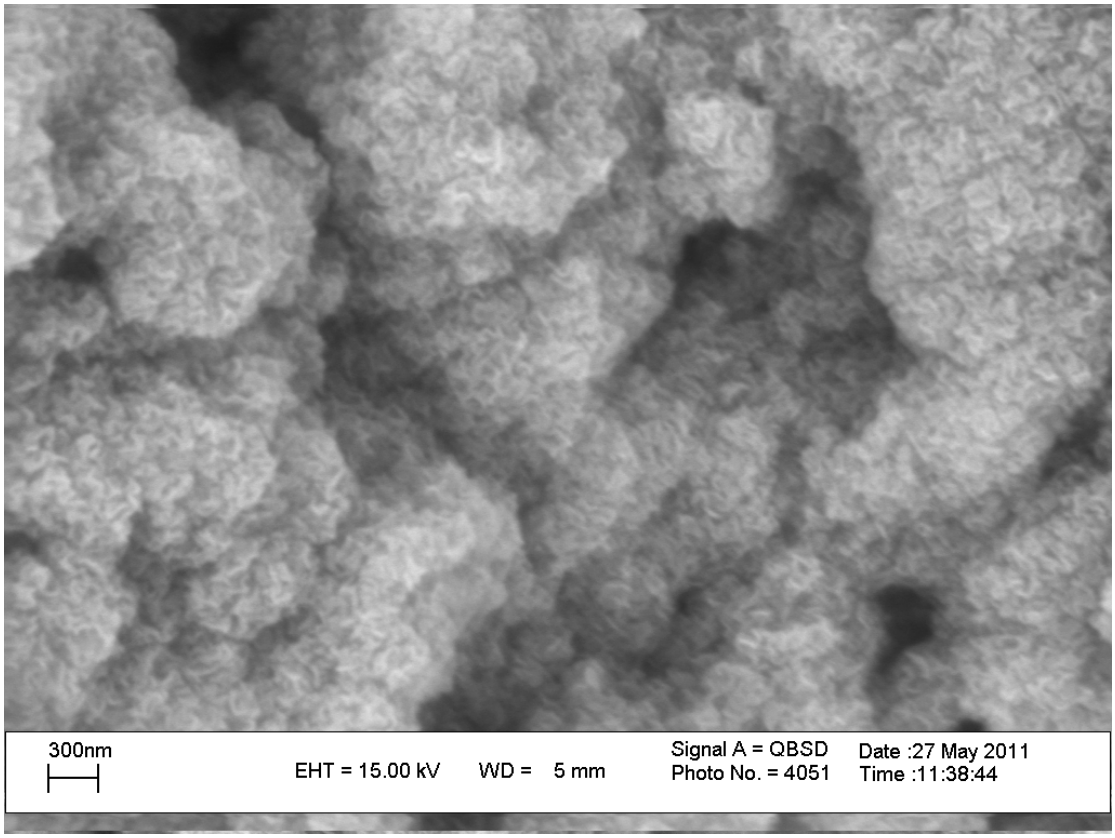


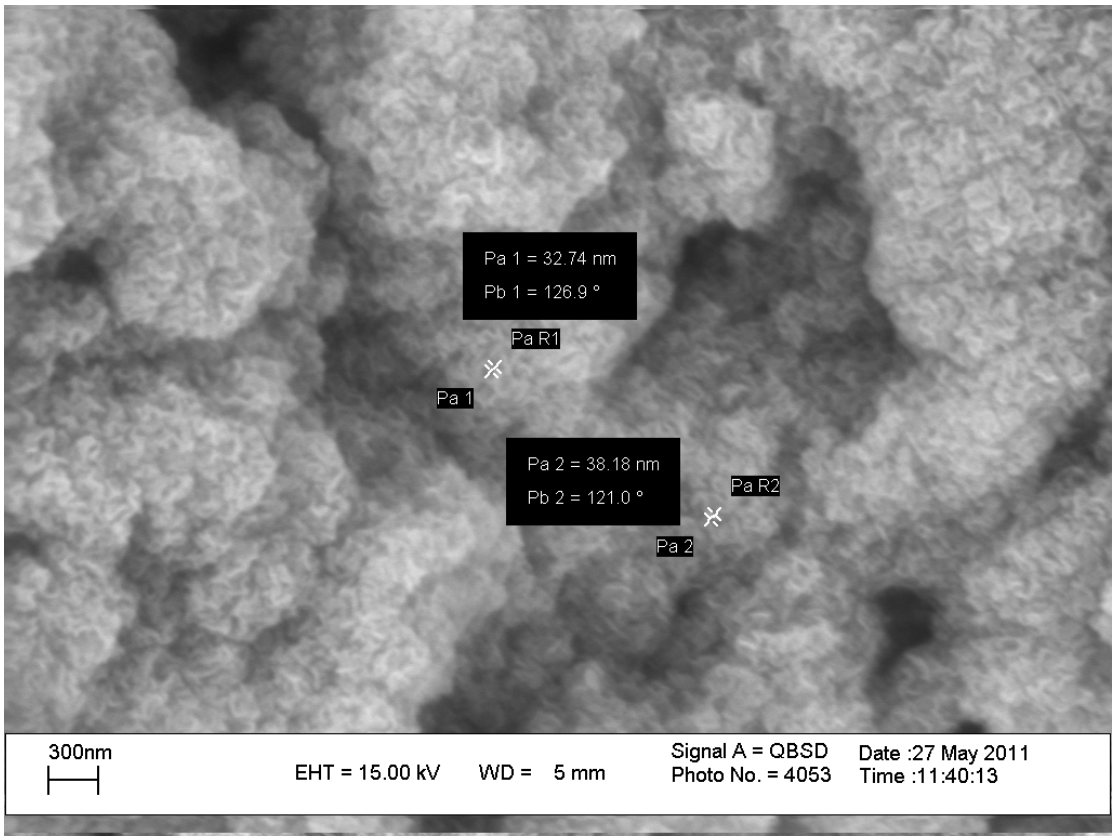


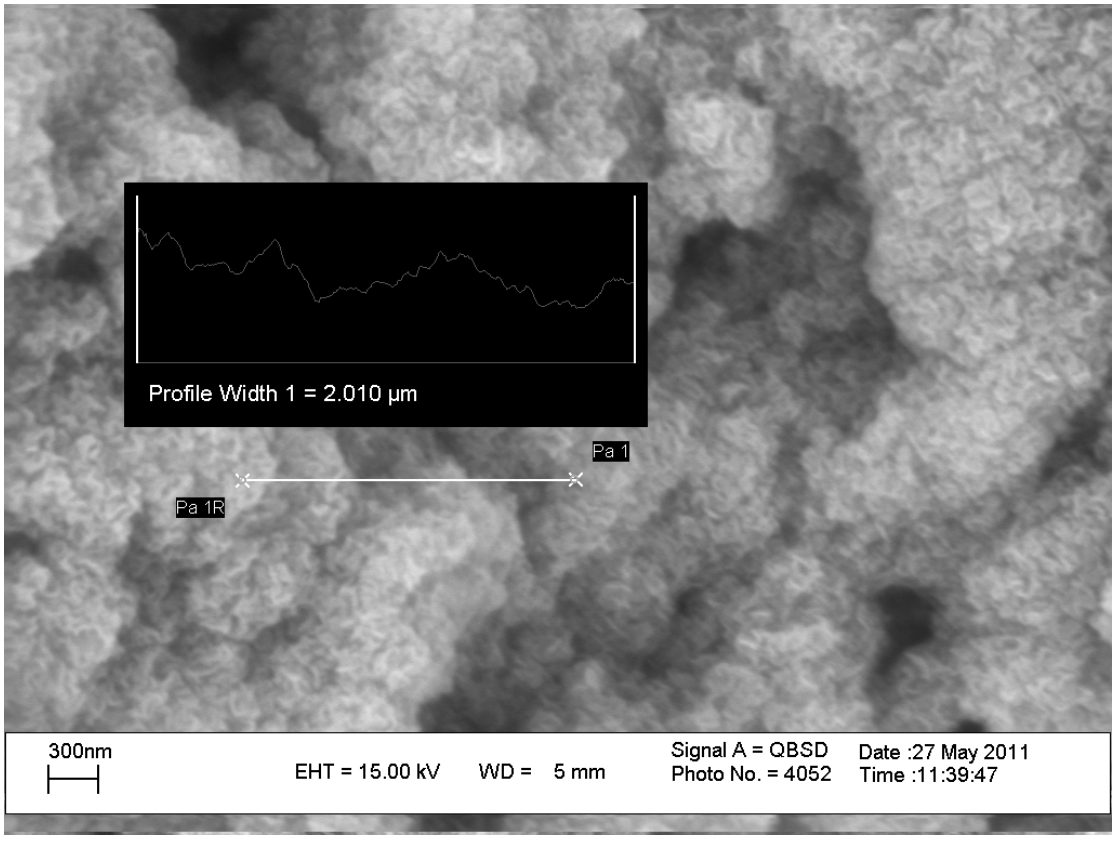












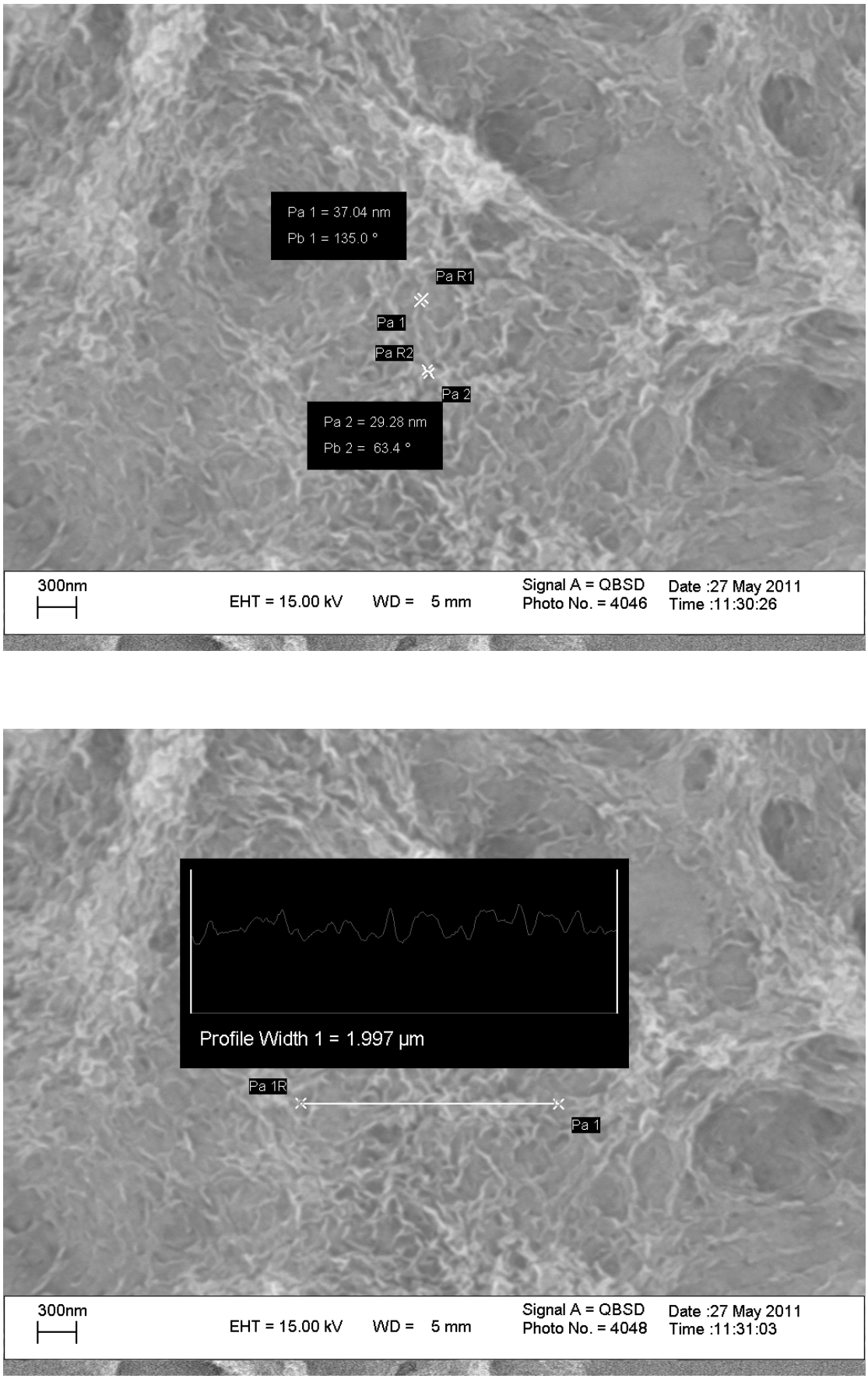
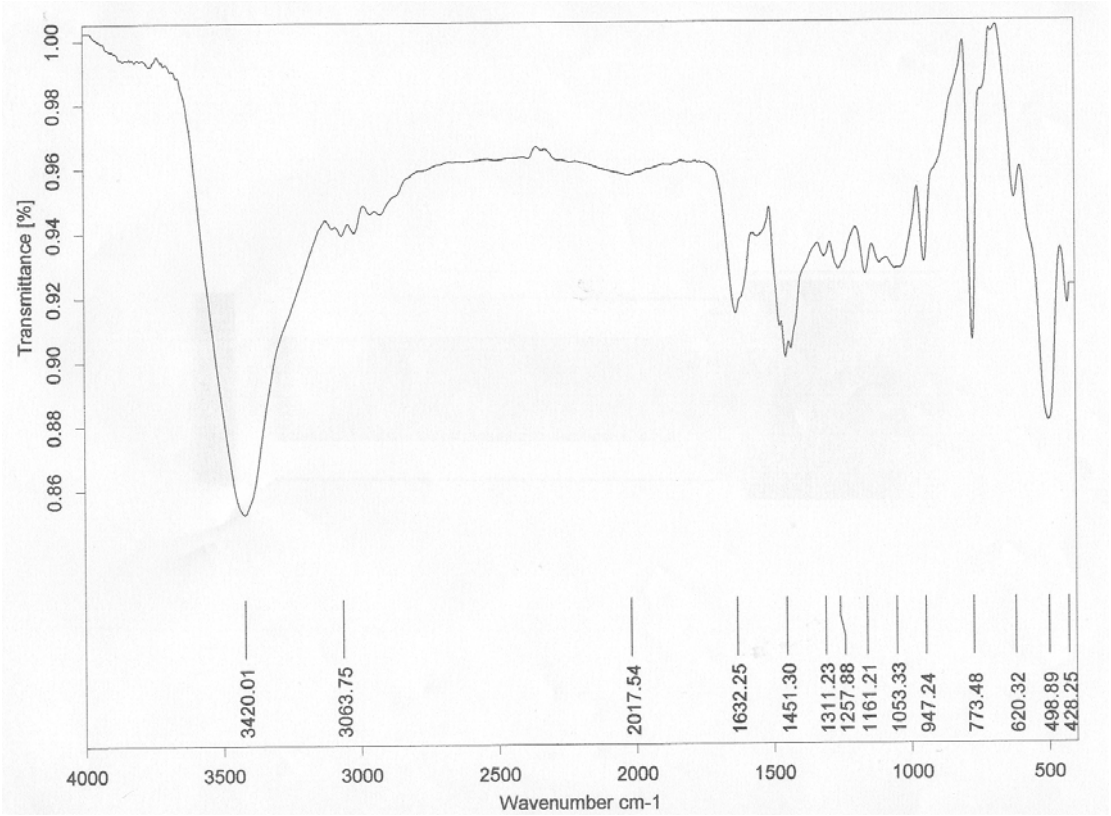
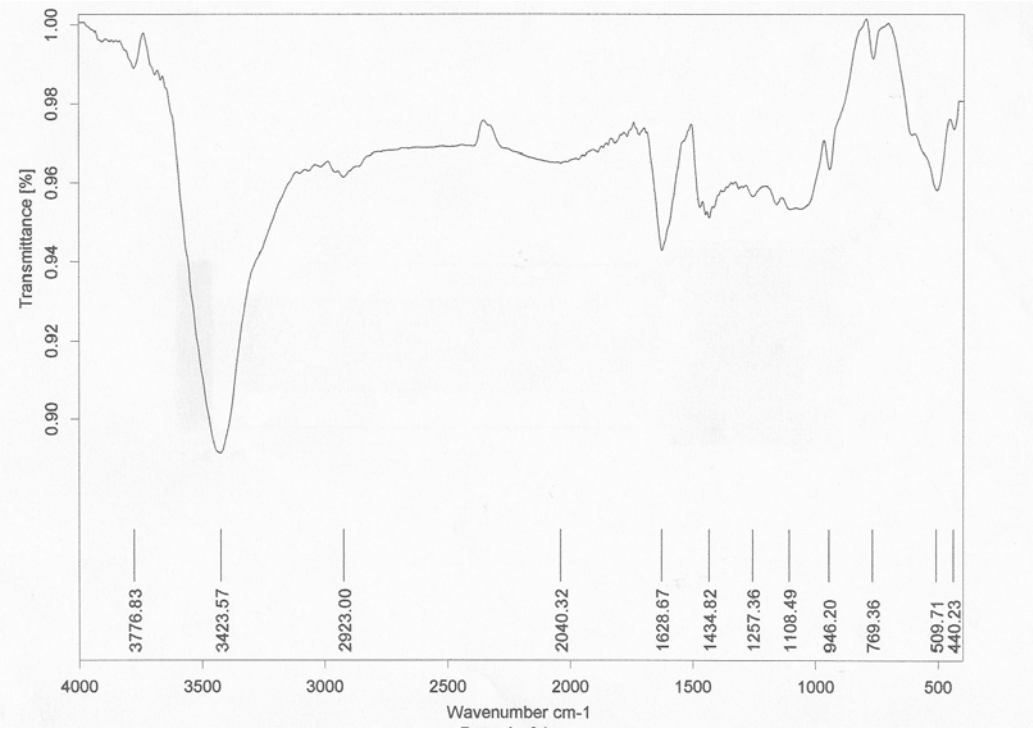


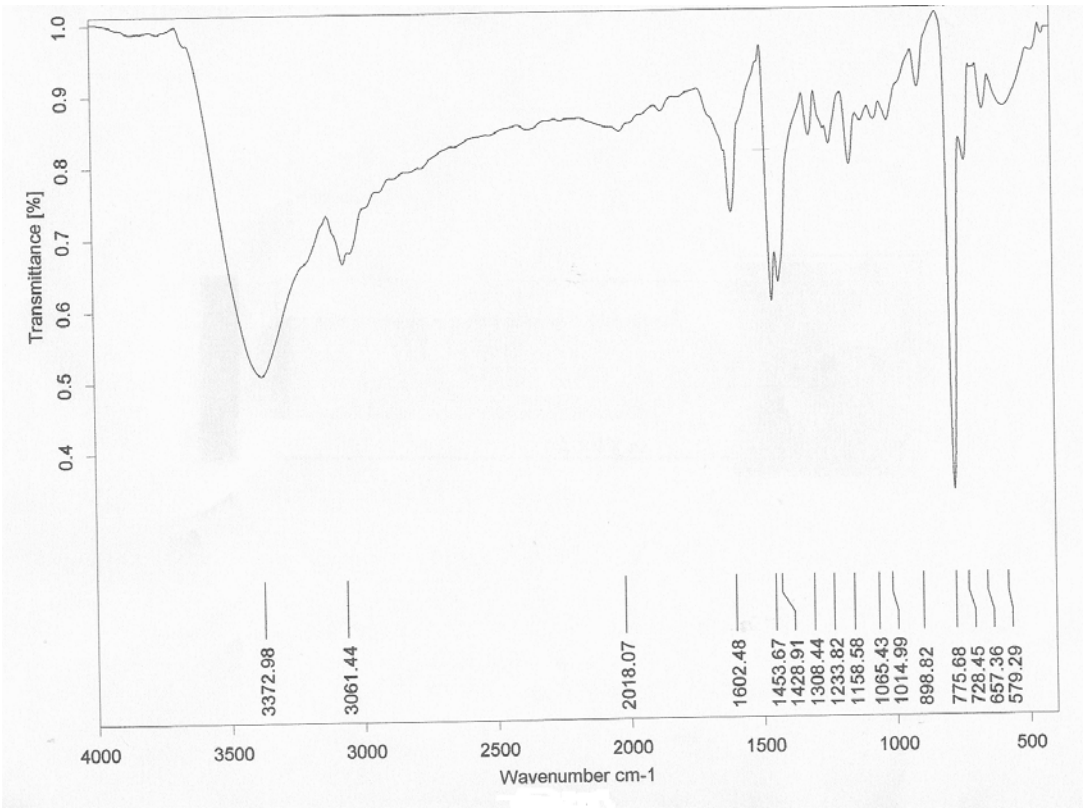
Fig. S7. SEM images of **1**.



a



b



c

Fig. S8. MIR spectra of self-assembled layered hybrid $[Ru(bpy)_3]^{2+}$/manganese (III, IV) oxide (**1**) (a) manganese (III),(IV) oxide monosheet (b) and $[Ru(bpy)_3]Cl_2$ (c). IR spectrum of **1** indicates the presence of both $[Ru(bpy)_3]^{2+}$ and manganese oxide in the structure.

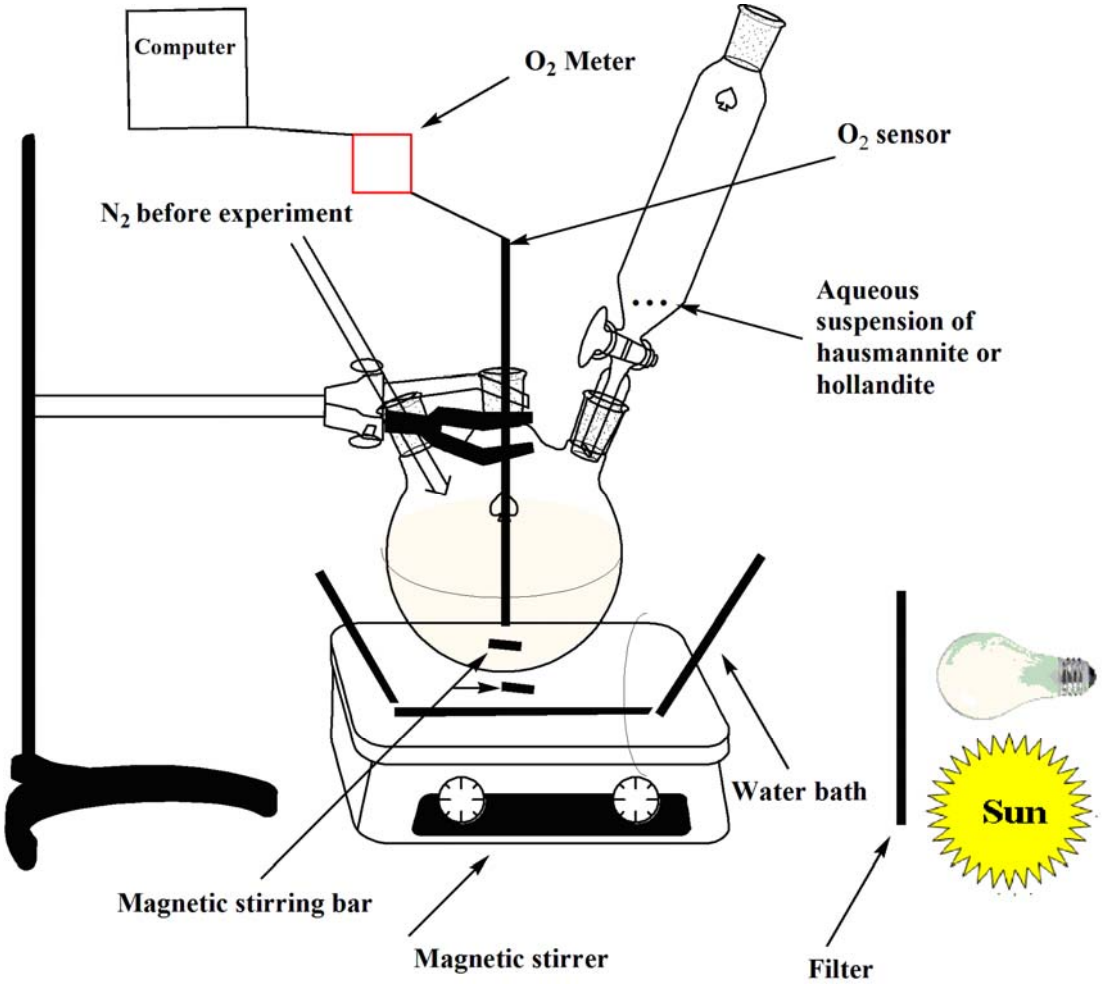


Fig. S9. The reactor set-up for oxygen evolution experiment from aqueous solution in the presence of tris(2,2'-bipyridyl)ruthenium(II) chloride, chloro pentaammine cobalt(III) chloride, in acetate buffer in the presence of light (from a bulb or sun) ($\lambda > 400$ nm).

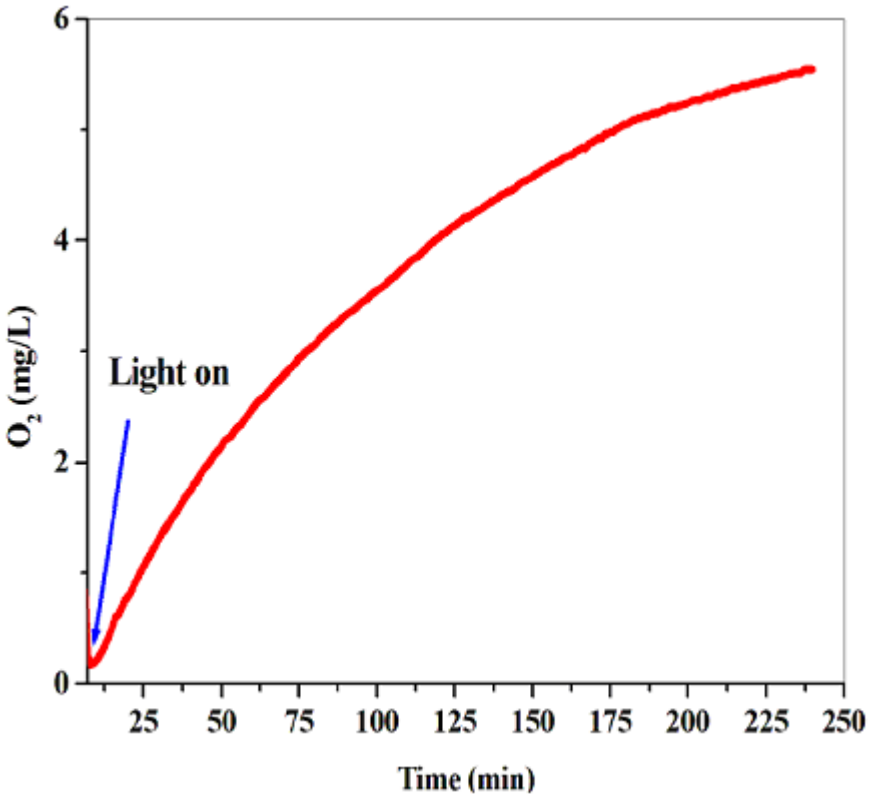
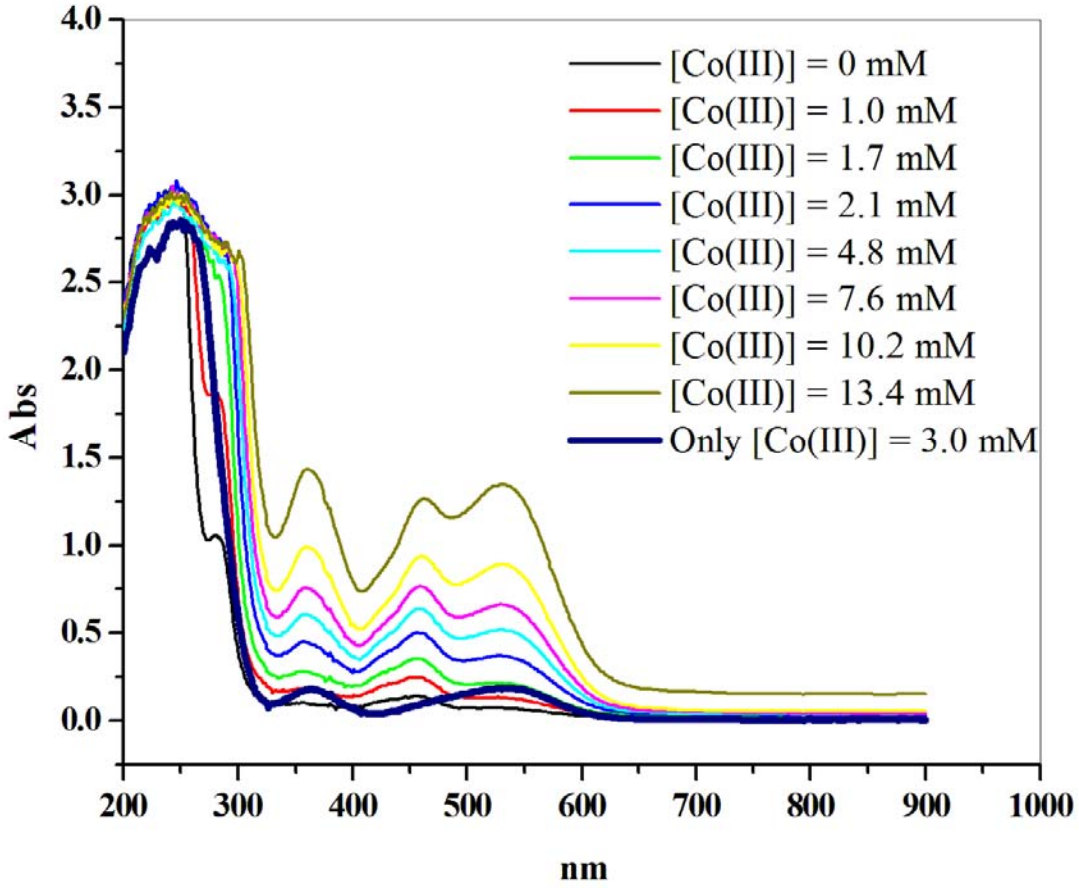
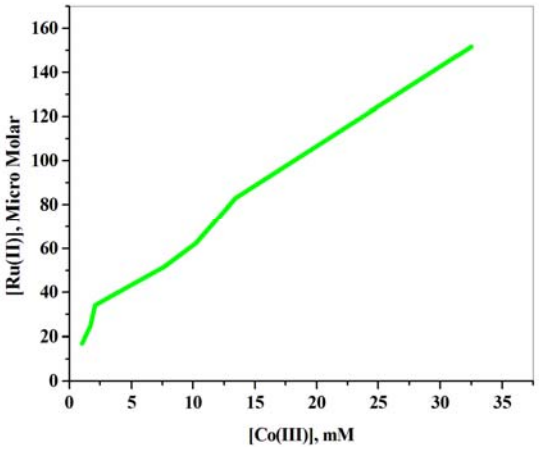


Fig. S10 Oxygen evolution in an aqueous solution in the presence of **1** (26.0 mg) at 25ºC. The intensity of light in this experiment was 5,000 lux with a 250W tungsten- mercury lamp that is much less than one twenth of a bright sunny day.



a



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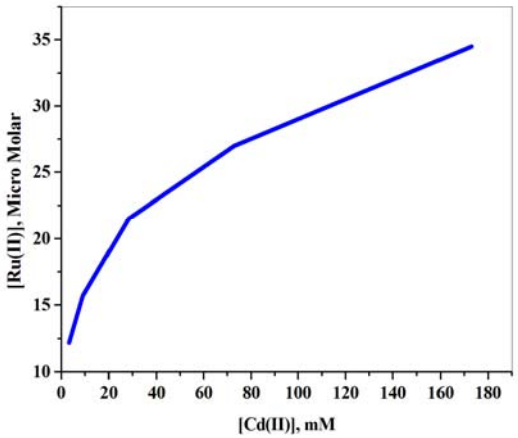

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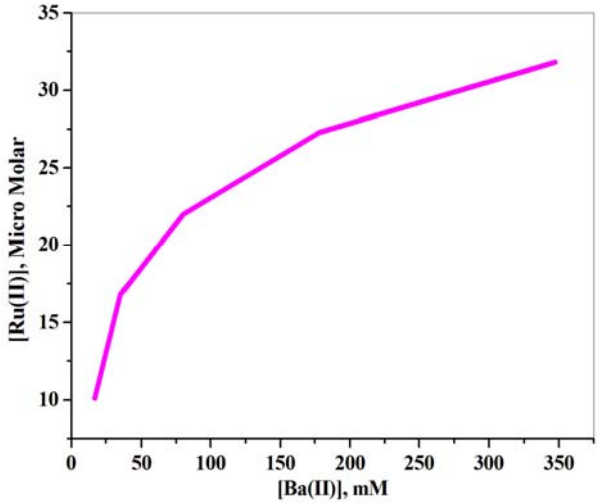
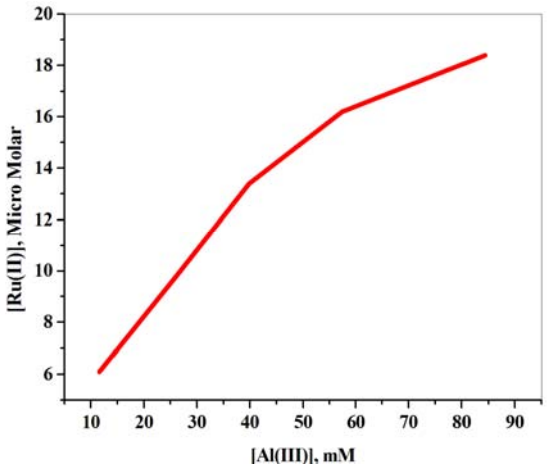
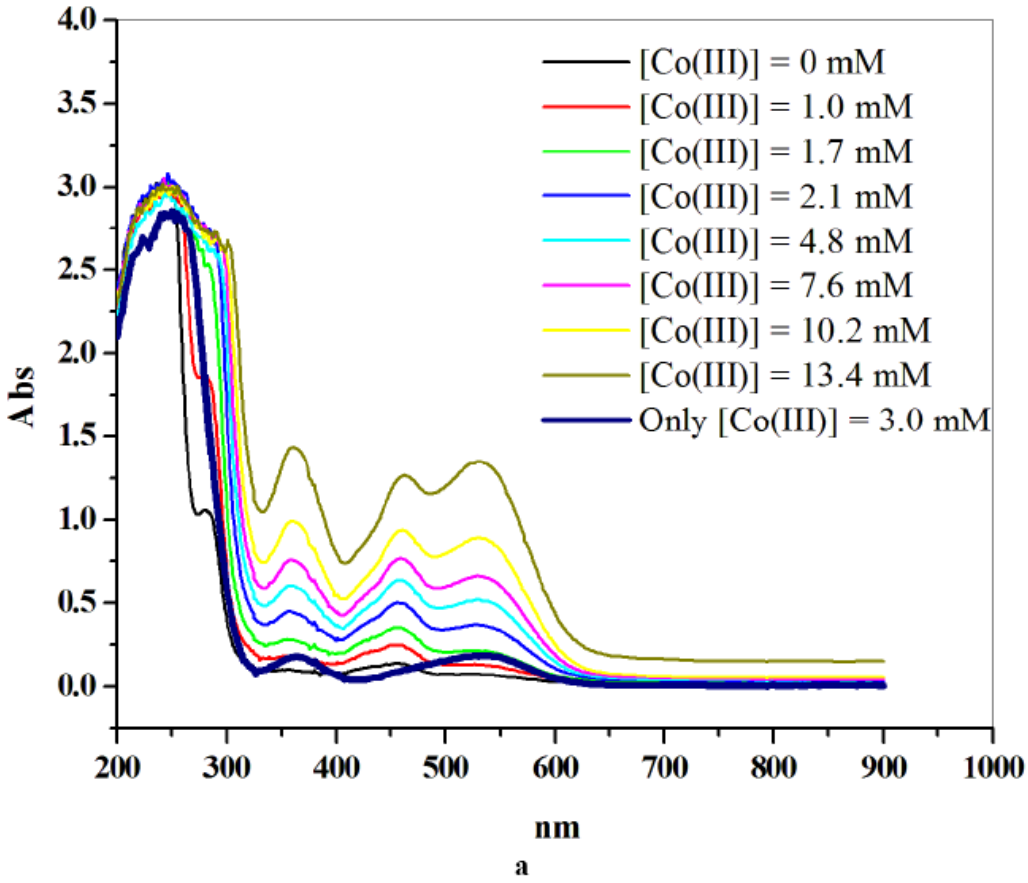


d



e

Fig. S11. UV-VIS spectra of resulting from **1** in the presence few different cations. a, UV-VIS spectra of resuting from **1** (3.0 mg) in a solutions (4.0 mL) of $[Co(NH_3)_5Cl]Cl_2$ with different concentrations in dark. The relations between concentration of $[Co(NH_3)_5Cl]Cl_2$ / $[Ru(bpy)_3]^{+2}$ (b), Cd(II) / $[Ru(bpy)_3]^{+2}$ (c), Ba(II) / $[Ru(bpy)_3]^{+2}$ (d), Al(III) / $[Ru(bpy)_3]^{+2}$ (e) for 3.0 mg from 1 (total volume of solution was 4.0 mL).



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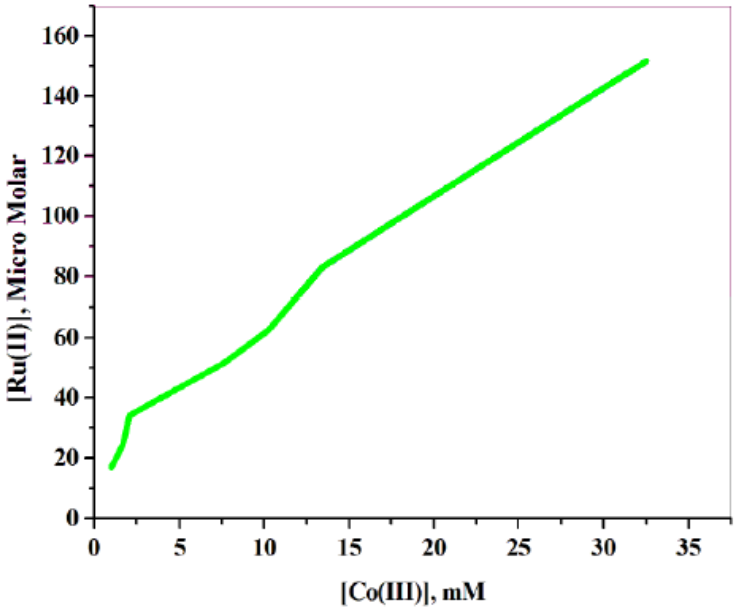
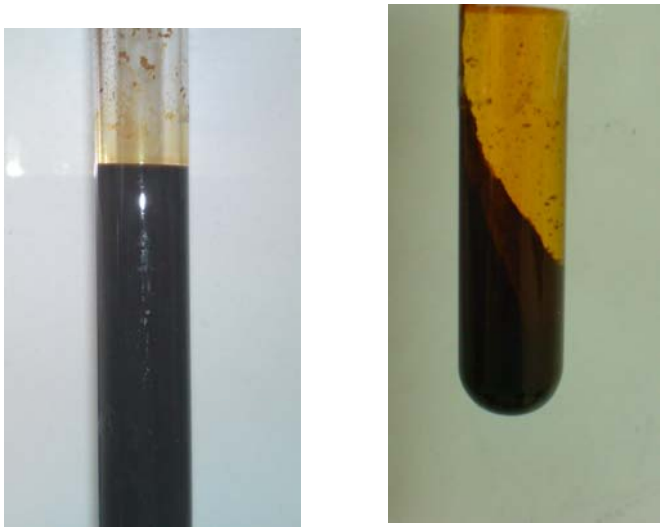


b

Fig. S12. UV-VIS spectra of resulting from **1** (3.0 mg) in a solutions (4.0 mL) of $[Co(NH_3)_5Cl]Cl_2$ with different concentrations in dark (a). The relations between concentrations of $[Co(NH_3)_5Cl]Cl_2$ and $[Ru(bpy)_3]^{+2}$ in solution for 3.0 mg from **1** (total volume of solution was 4.0 mL) (b).



a b

Fig. S13. Photographs of brown colloidal suspension of manganese (III, IV) monosheets (a) and compound **1** precipitated by adding a $[Ru(bpy)_3]Cl_2$ aqueous solution to the colloidal suspension of manganese (III, IV) monosheets (b).

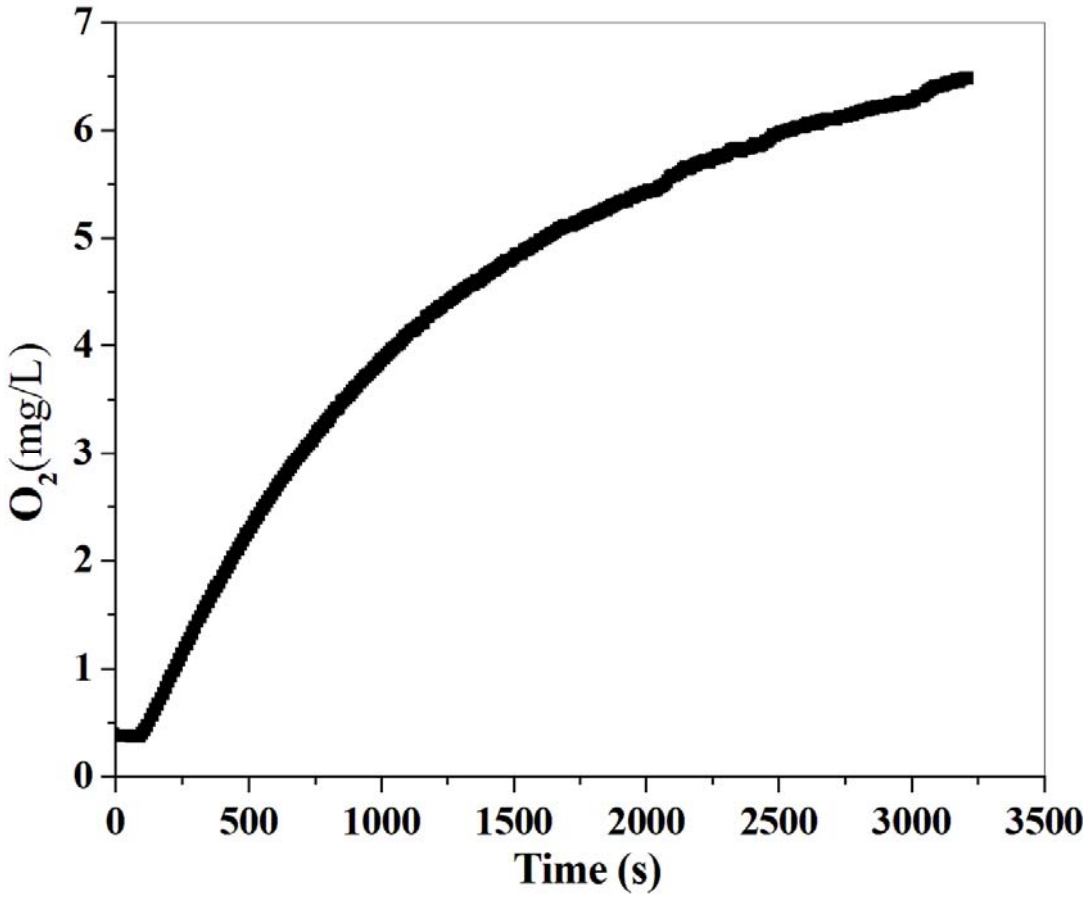


Fig. S14. Oxygen evolution in an aqueous solution of 0.23 M Ce(IV) at 28.2ºC in the presence of dried manganese (III, IV) oxide monosheets (26.0 mg). Without catalyst, Ce(IV) was stable in this condition and oxygen evolution was not observed.

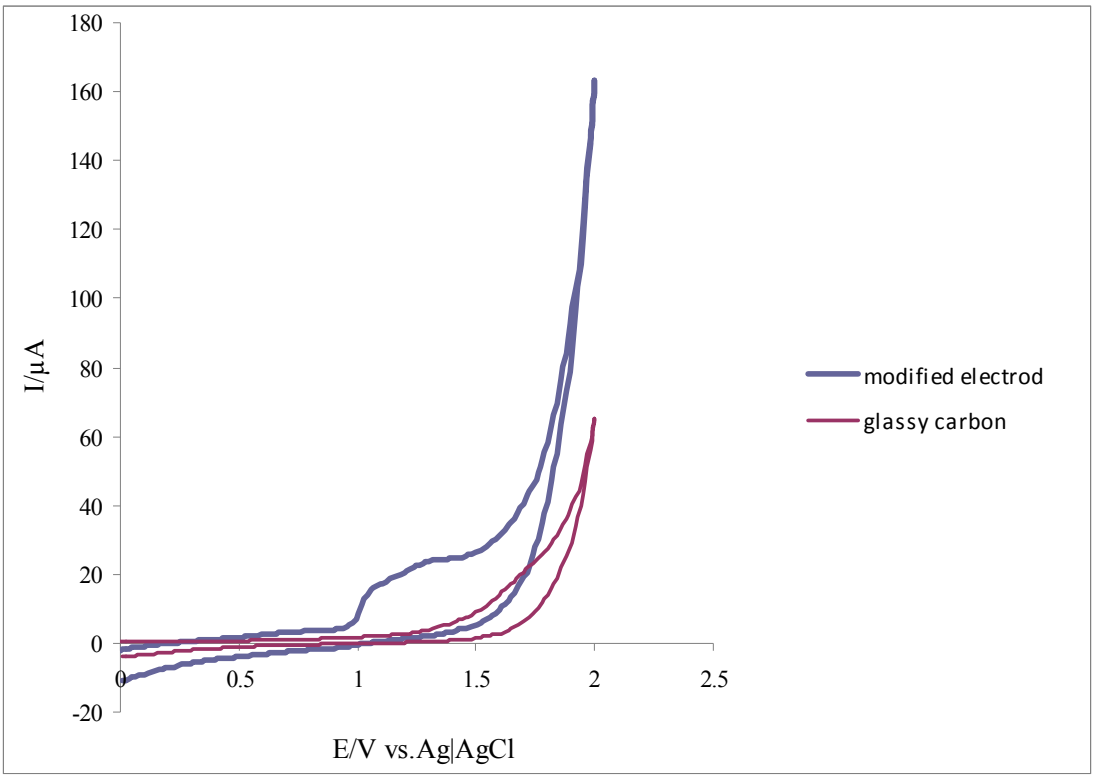


Fig. S15. Cyclic voltammograms (CVs) of a glassy carbon electrode and glassy carbon electrode modified with dried manganese (III, IV) oxide monosheets in lithium perchlorate solution (0.1 M in water, pH=6.3) at a scan rate of 50 mV s^{-1} (vs. Ag|AgCl).

Reference:

1. Kai, K., Yoshida Y., Kageyama, H., Saito, G., Ishigaki, T., Furukawa, Y. & Kawamata, J. Room-temperature synthesis of manganese oxide monosheets. *J. Am. Chem. Soc.* **130**, 15938-15943 (2008).