Electronic Supplementary Material (ESI) for Chemical Communications

Nanolayered manganese oxide / Poly (4-vinylpyridine) as a biomimetic and very efficient water oxidizing catalyst: Toward an artificial enzyme in artificial photosynthesis

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Table of Contents

Experimental Section

Synthesis

l-MnO_x-PVP: The compound was synthesized by a very simple method. In brief, to a suspension of PVP (1 g) in water (10 mL) and 0.5 mL acetic acid, $Mn(OAC)_2$ (50 mg) was added and stirred for 1 h under Ar. Then, a solution of $KMnO_4$ (6 mg) in water (5 mL) containing KOH (50 mg) was added to the suspension with vigorous stirring at room temperature under argon. After evaporating water l-MnO_x-PVP film was obtained. Mn%: 0.92

m-MnO_x-PVP: In brief, to a suspension of PVP (1 g) in water (10 mL) and 0.5 mL acetic acid, $Mn(OAC)_2$ (100 mg) was added and stirred for 1 h under Ar. Then a solution of $KMnO_4$ (12 mg) in water (5 mL) containing KOH (50 mg) was added to the suspension with vigorous stirring at room temperature under argon. After evaporating water m-MnO_x-PVP film was obtained. Mn%: 2.02

h-MnO_x-PVP: In brief, to a suspension of PVP (1 g) in water (10 mL) and 0.5 mL acetic acid, was added $Mn(OAC)_2$ (2000 mg) and stirred for 1 h under Ar. Then a solution of $KMnO_4$ (120 mg) in water (5 mL) containing KOH (500 mg) was added to the suspension with vigorous stirring at room temperature under argon. After evaporating water h-MnO_x-PVP film was obtained. Mn%: 10.58.

Characterization

MIR spectra of KBr pellets of compounds were recorded on a Bruker vector 22 in the range between 400-4000 cm^{-1}. TEM, EDX and SEM images were obtained with Philips CM120, VEGA\TESCAN-XMU and LEO 1430VP, respectively. The X-ray powder patterns were recorded with a Bruker, D8 ADVANCE (Germany) diffractometer (Cu-Kα radiation). Mn atomic absorption spectroscopy (AAS) was performed on an Atomic Absorption Spectrometer

Varian Spectr AA 110. Prior to analysis, the oxide (2.0 mg) were added to concentrated nitric acid and H_2O_2, left at room temperature to ensure that the oxides were completely dissolved. The solutions were then diluted to 50.0 or 100.0 mL and analysed by AAS.

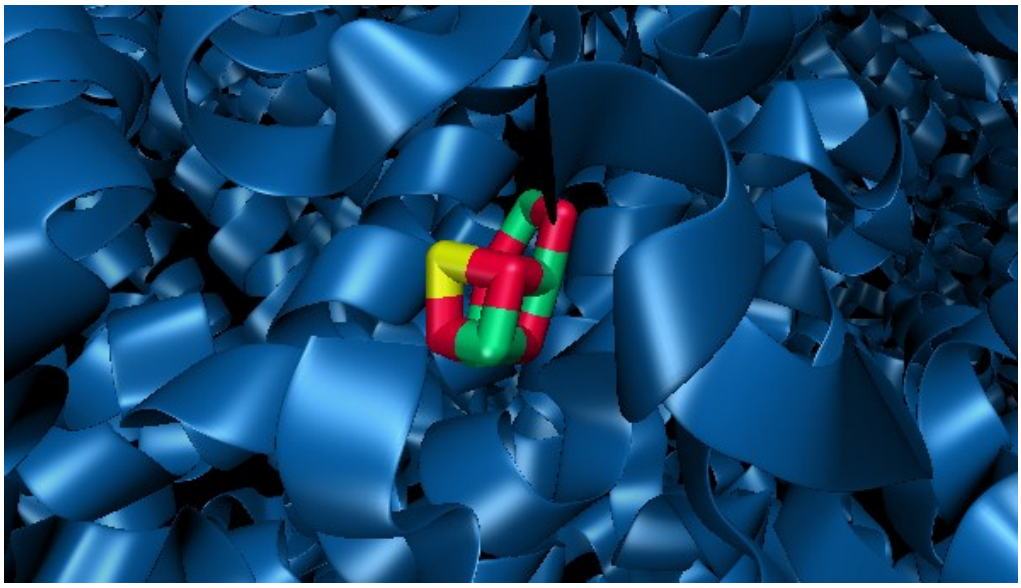
Cyclic voltammetry and amperometric studies were performed using an Autolab potentiostat-galvanostat model PGSTAT30 (Utrecht, The Netherlands). In this case a conventional three electrode set-up was used in which a Pt electrode or Pt electrode modified with MnO_x-PVP, a $Ag|AgCl|KCl_{sat}$ electrode 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.

Fabrication of modified electrode

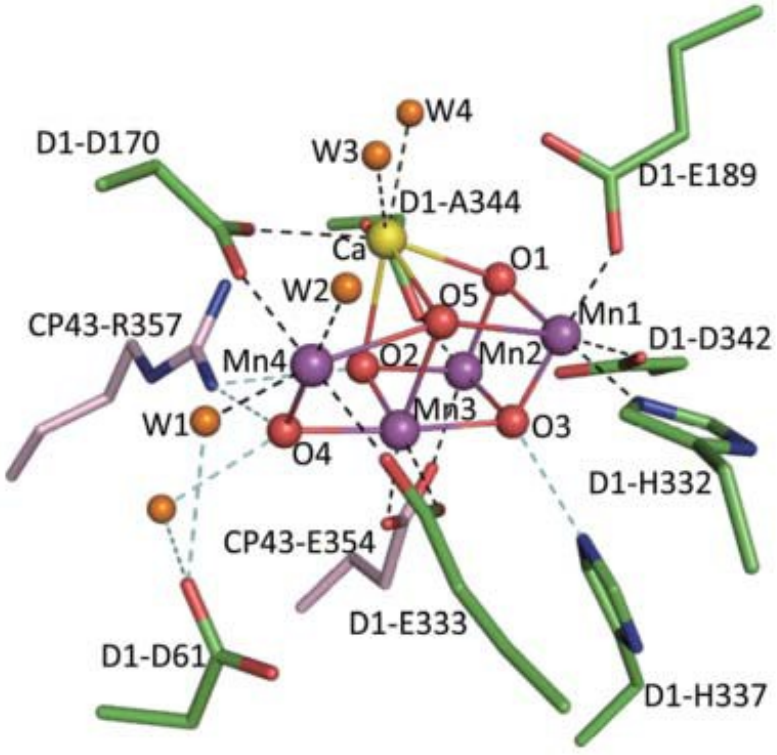
The Pt electrode was mechanically polished with 1, 0.3 and 0.05 μm alumina and washed ultrasonically with ethanol and distilled water. Then, 30 μL of compound (l-MnO_x-PVP, m-MnO_x-PVP and h-MnO_x-PVP) suspension was dripped on the Pt electrode surface and dried at room temperature. Eventually, 10μL of 0.5 wt % Nafion solution was deposited onto the center of the modified electrode. A three-electrode system was applied for investigation of electrochemical properties of modified electrodes by cyclic voltammetry, linear sweep voltammetry, and amperometry in a 0.1M pH 6.3 lithium perchlorate solution.

Water Oxidation

Oxygen evolution from aqueous solutions was measured using an HQ40d portable dissolved oxygen meter connected to an oxygen monitor with digital readout. Set up for oxygen meter and electrochemical devise is shown in Fig. S2



a



b

Fig. S1 Mn_4CaO_5 cluster (Ca: yellow; Mn: green; O: red) in the surrounding amino acids (blue). The whole structure of the Mn_4CaO_5 cluster resembles a distorted chair, with the asymmetric cubane (the image was made with VMD and is owned by the Theoretical and Computational Biophysics Group, NIH Resource for Macromolecular Modeling and Bioinformatics, at the Beckman Institute, University of Illinois at Urbana-Champaign. The original data for Fig. 1 is from ref. 1 (PDB: 3ARC)) (a). There are only a small fraction of the residues that come in direct contact with the Mn-Ca cluster (image was modified from ref. 1) (b).

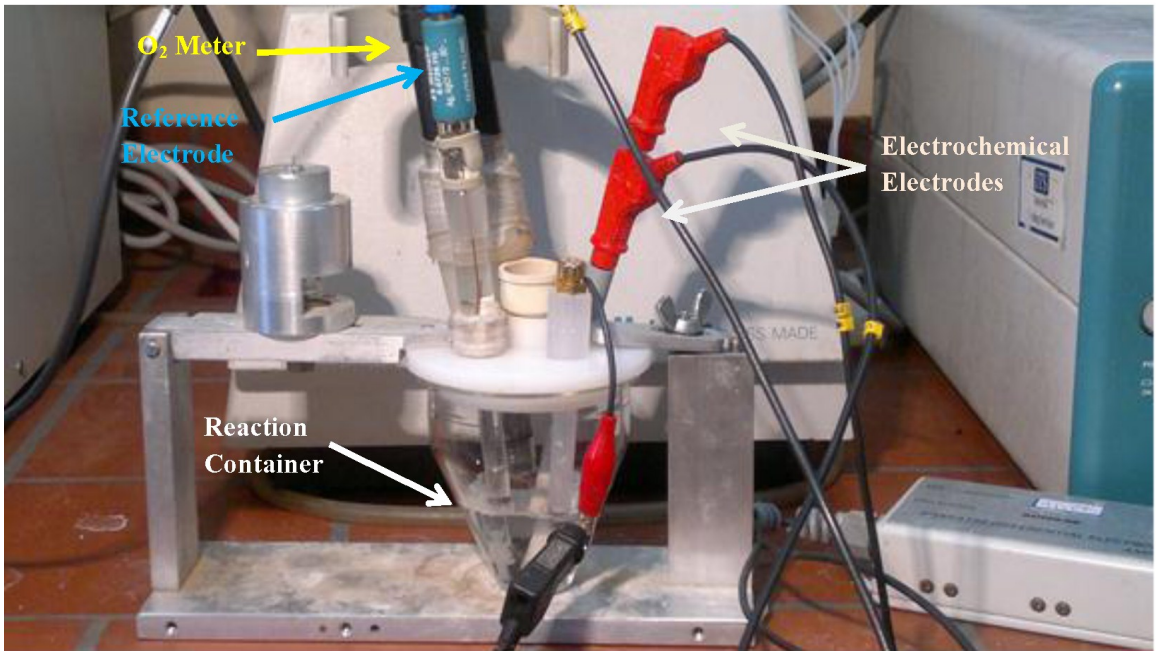
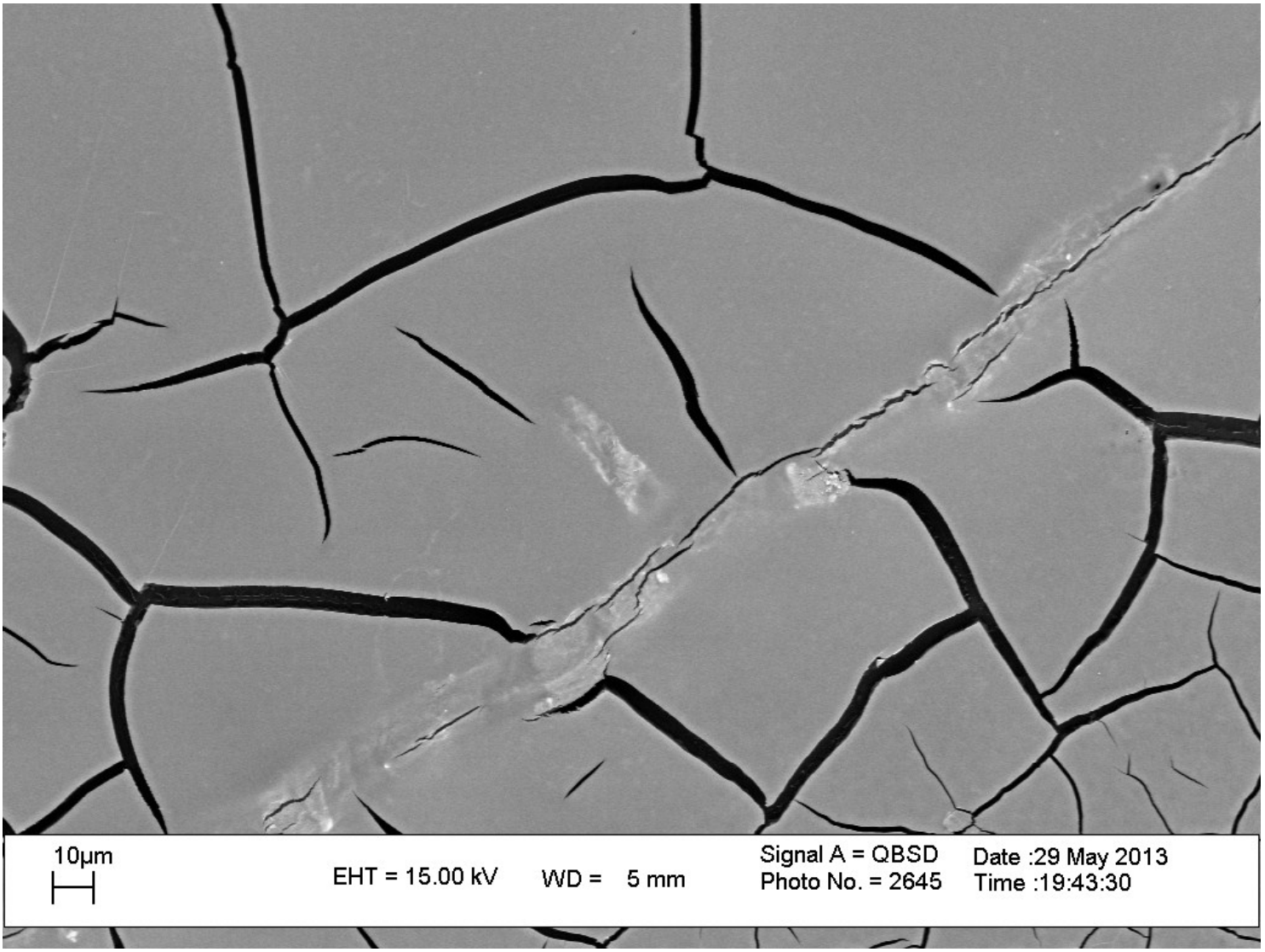


Fig. S2 Set up for electrochemical water oxidation.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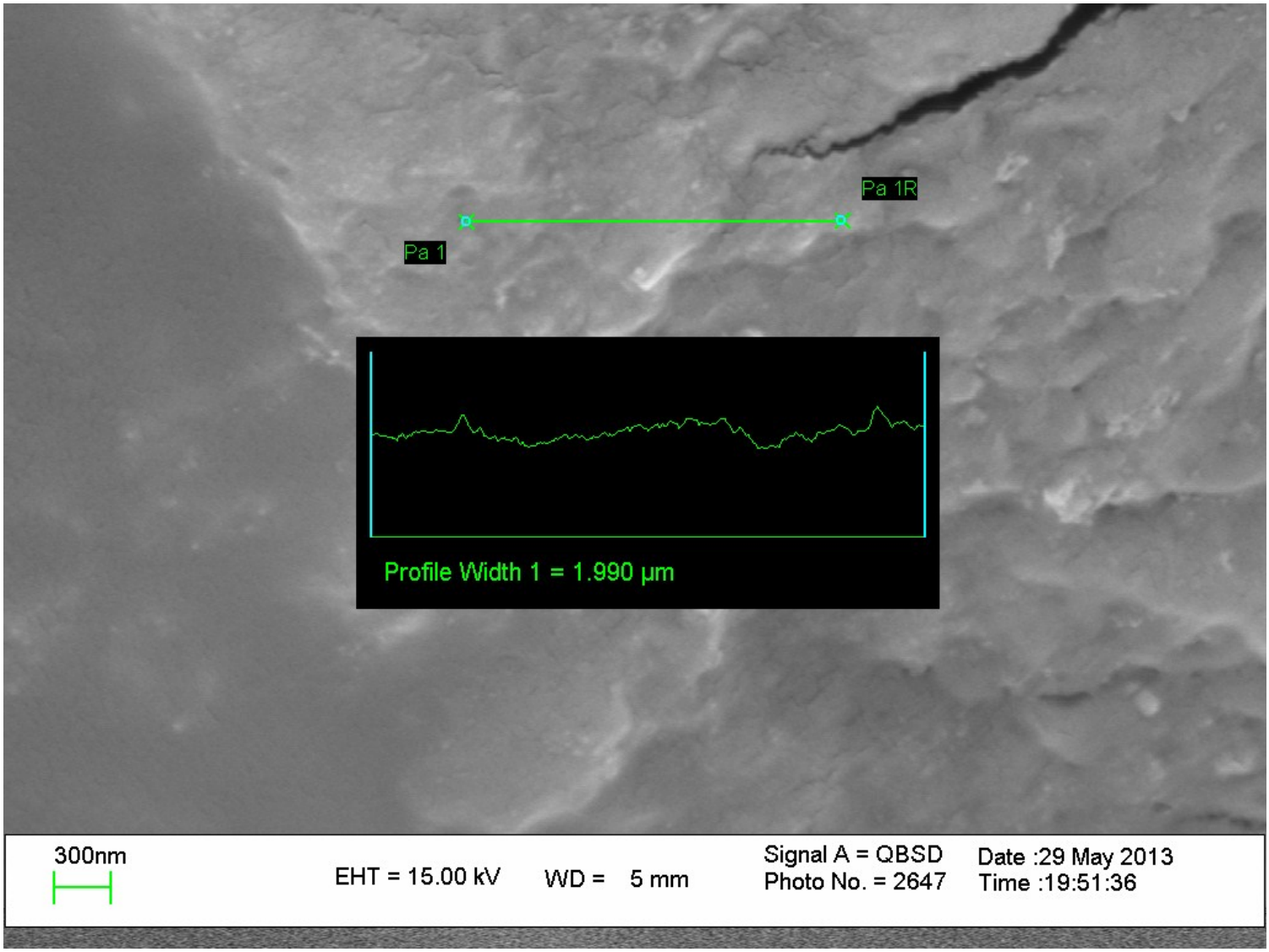
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 2645
Date :29 May 2013
Time :19:43:30

a



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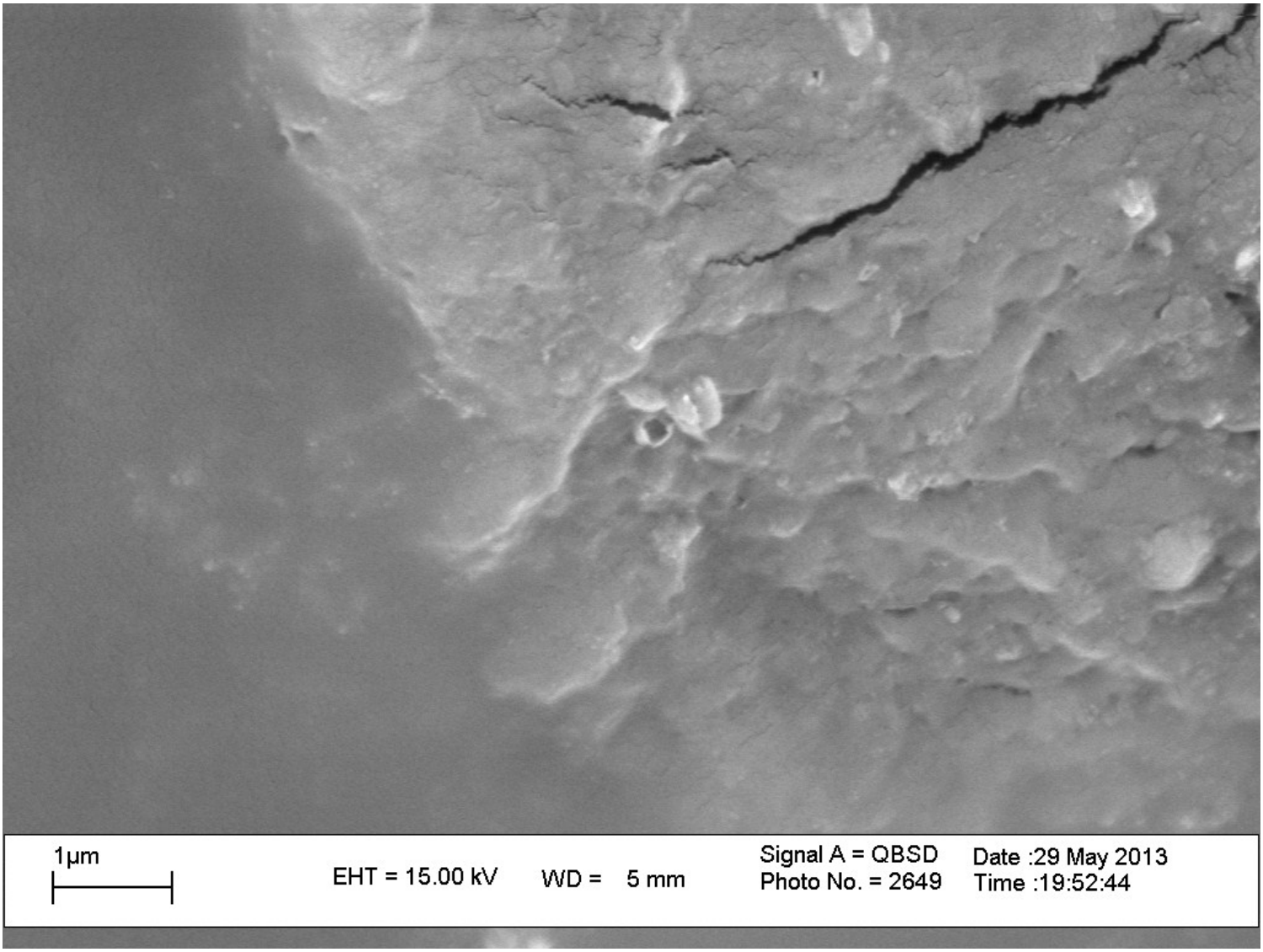

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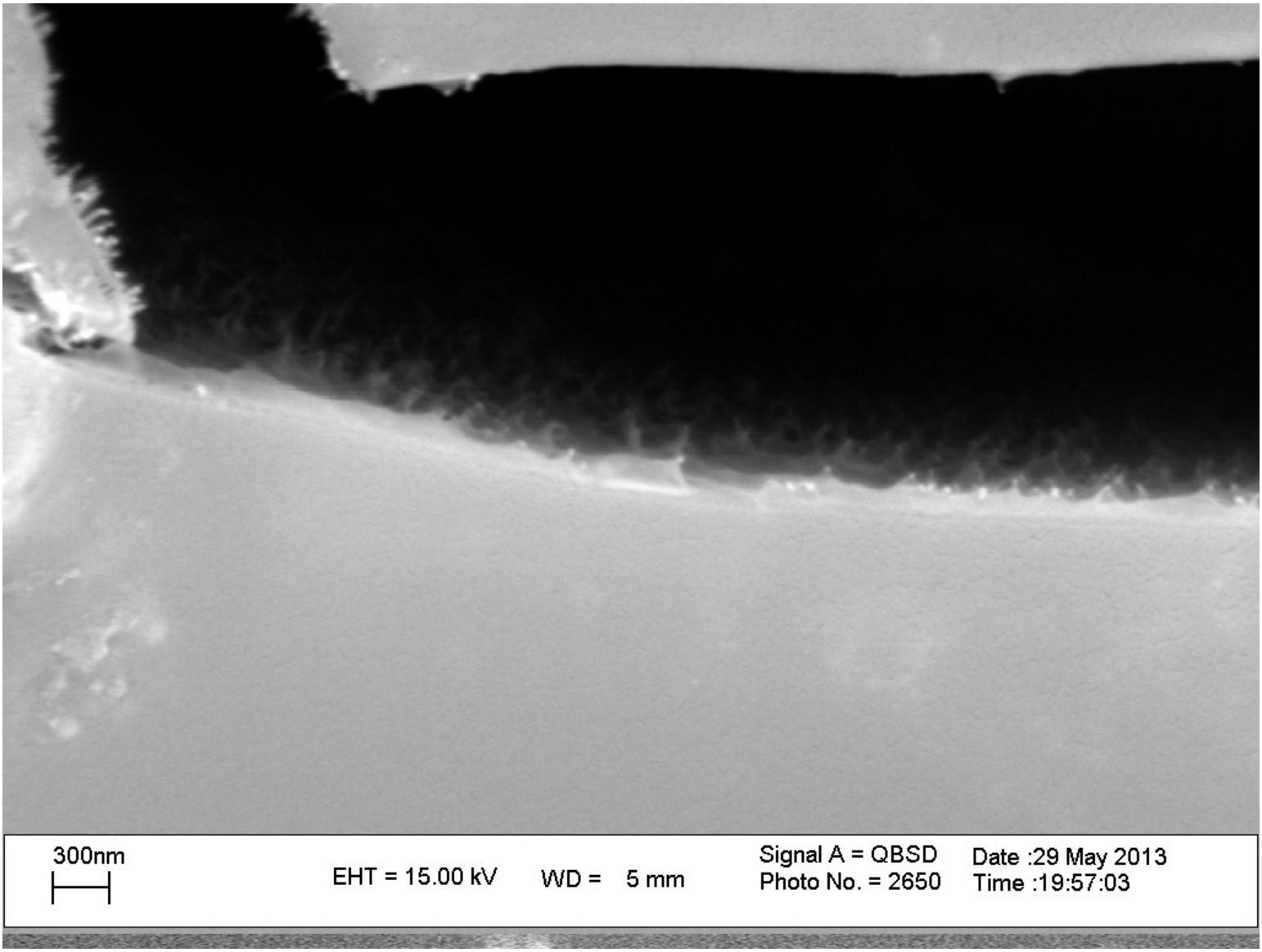
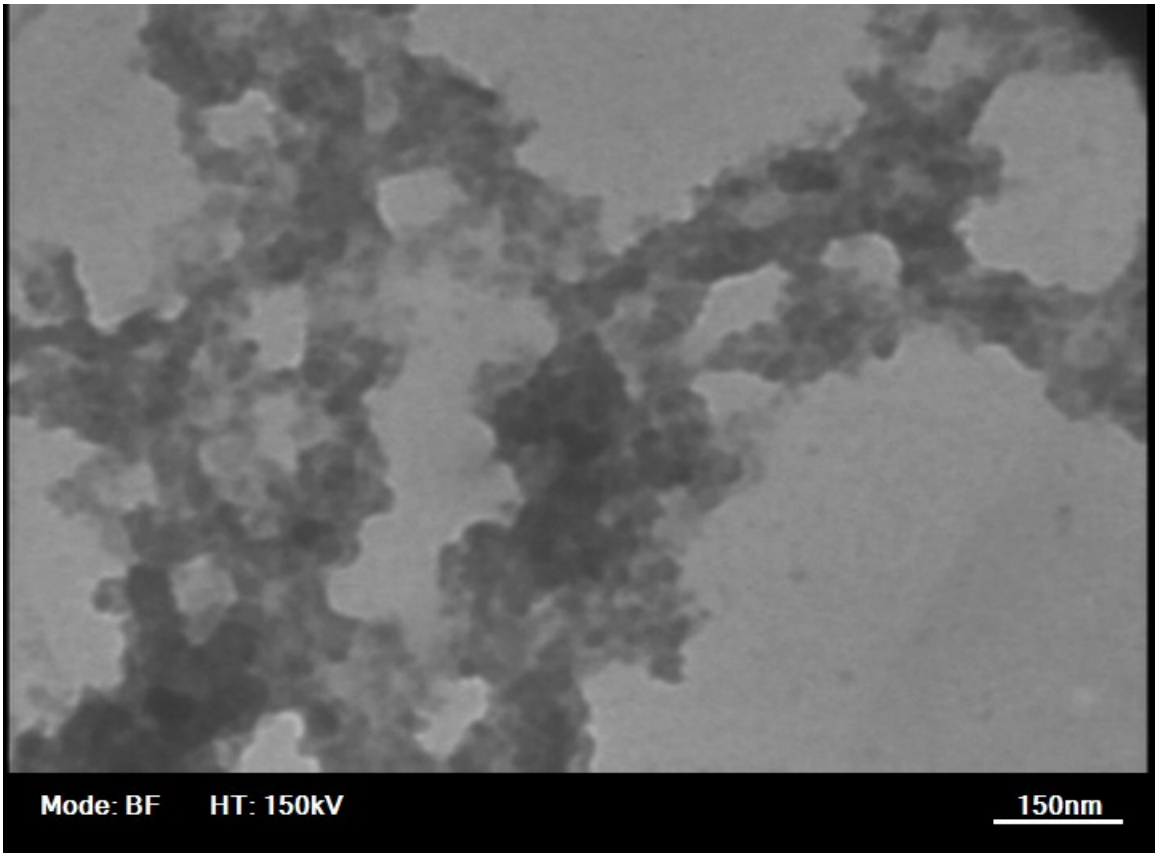
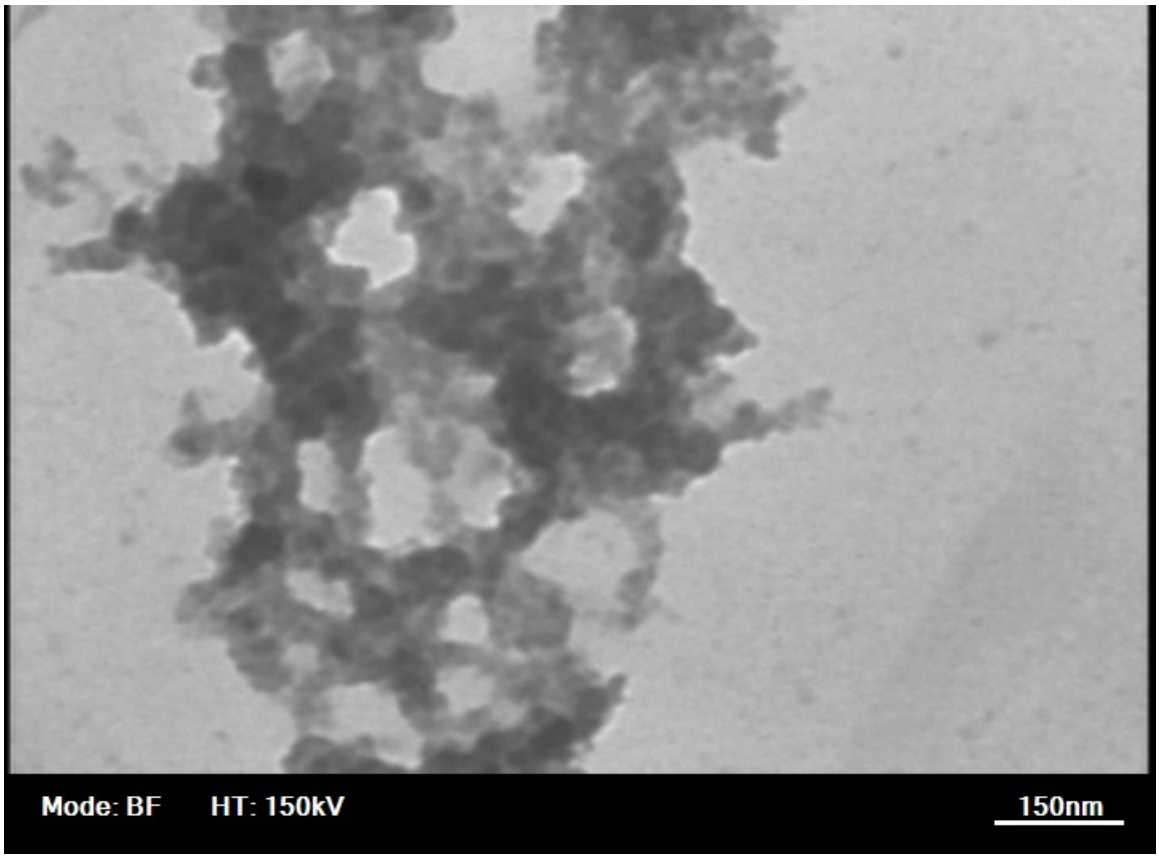


d

Fig. S3 SEM images of l-MnO_x-PVP (a-d).



a



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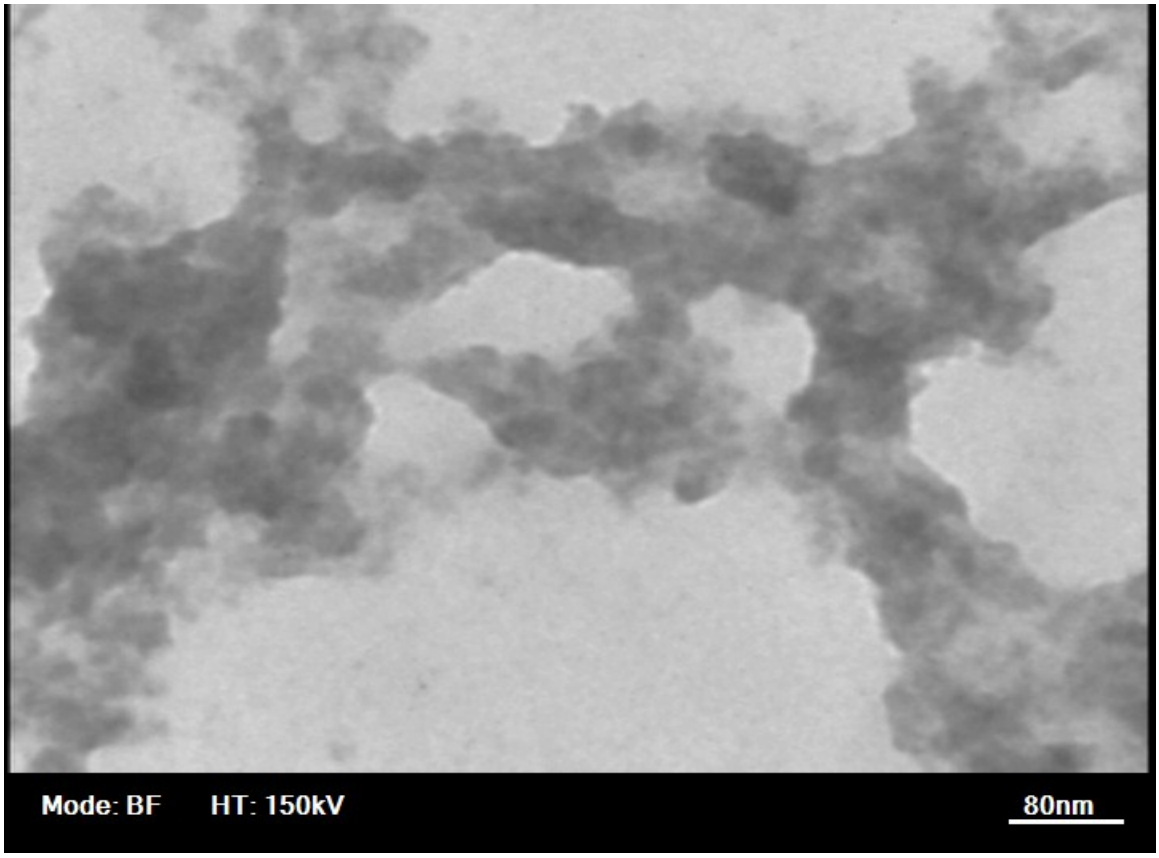

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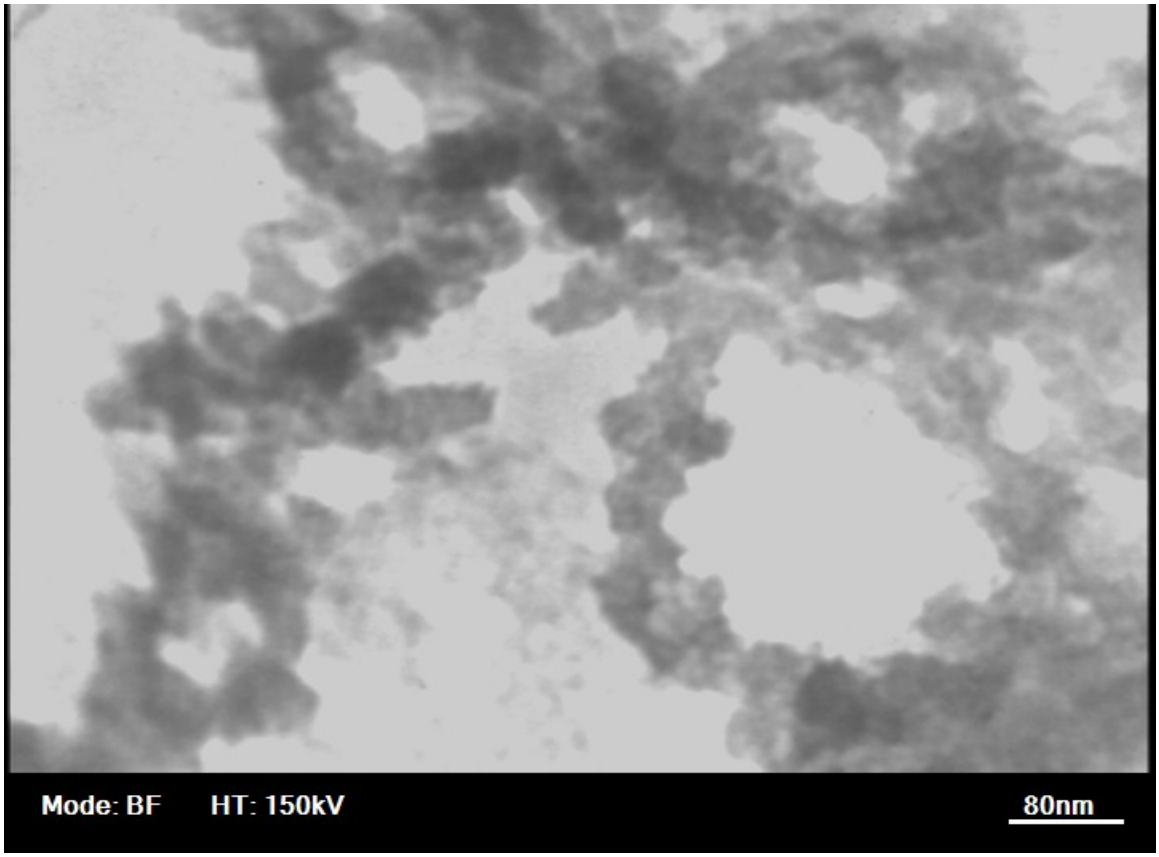

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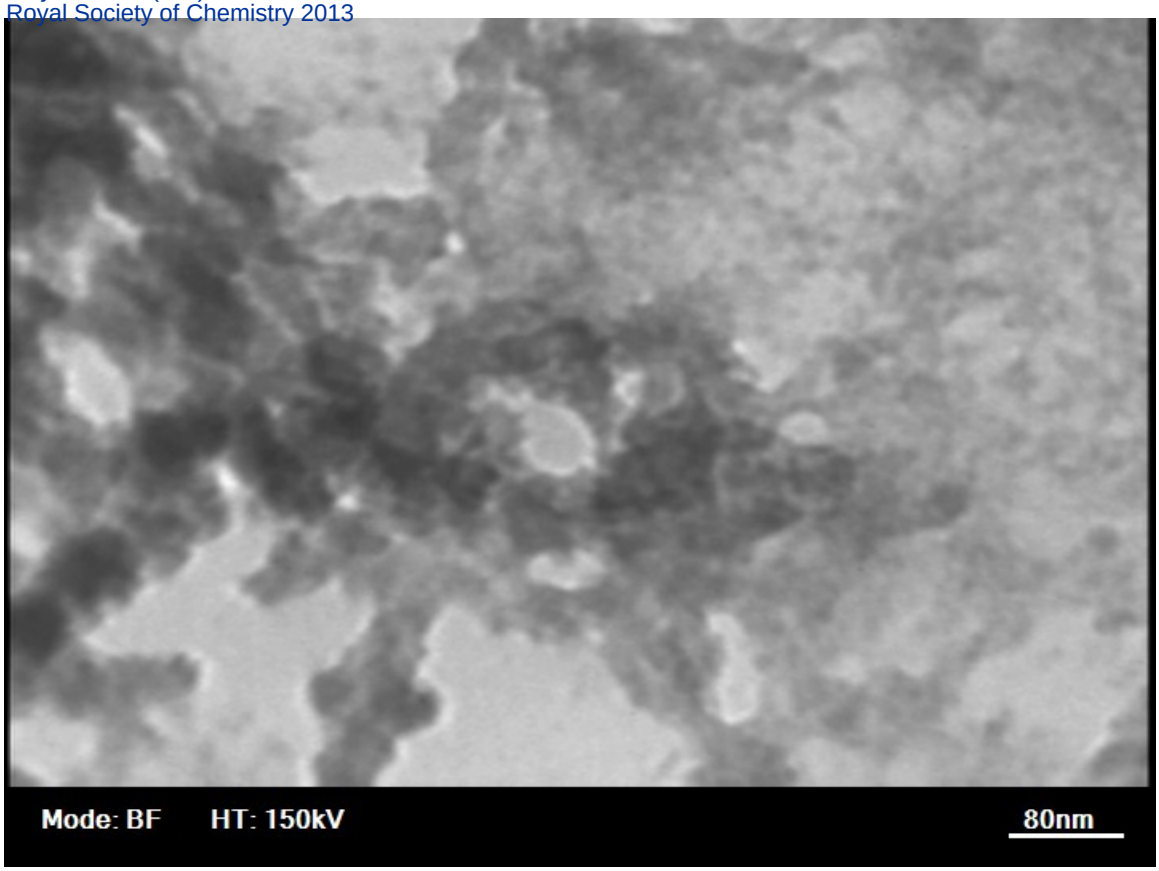

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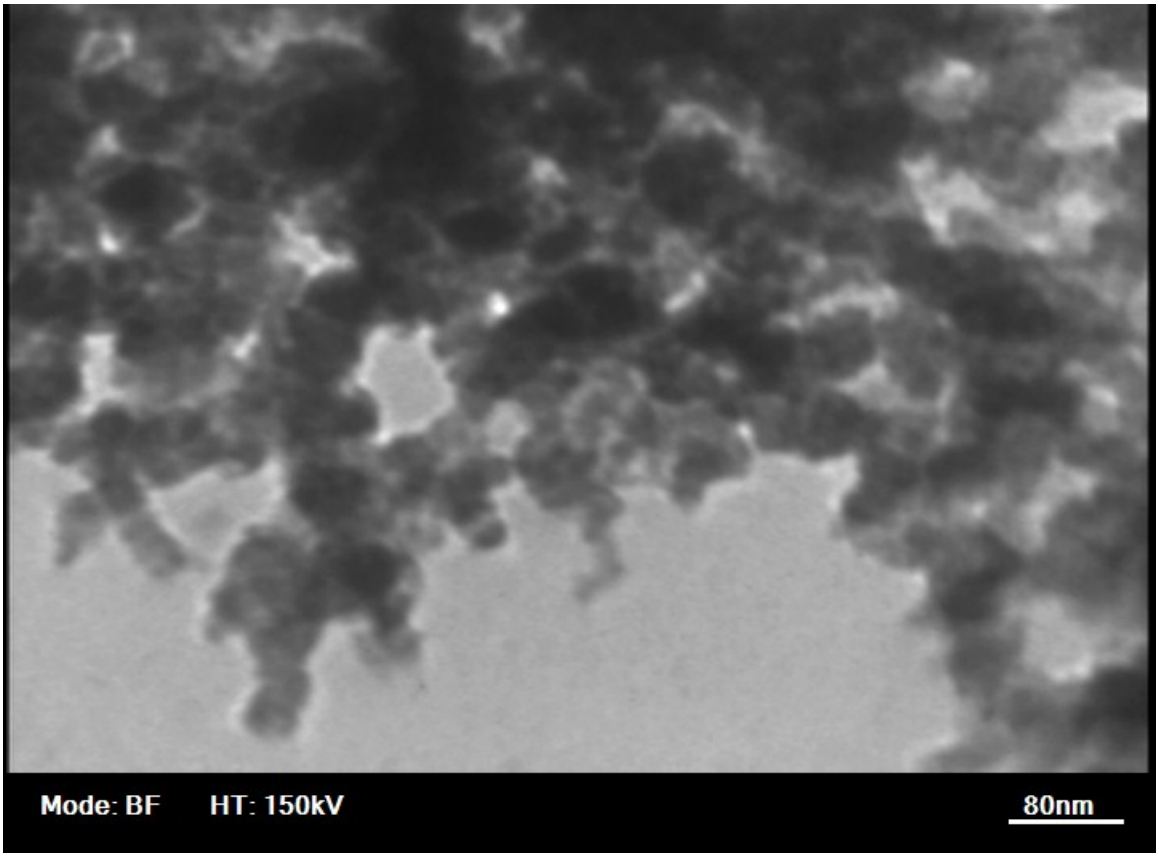

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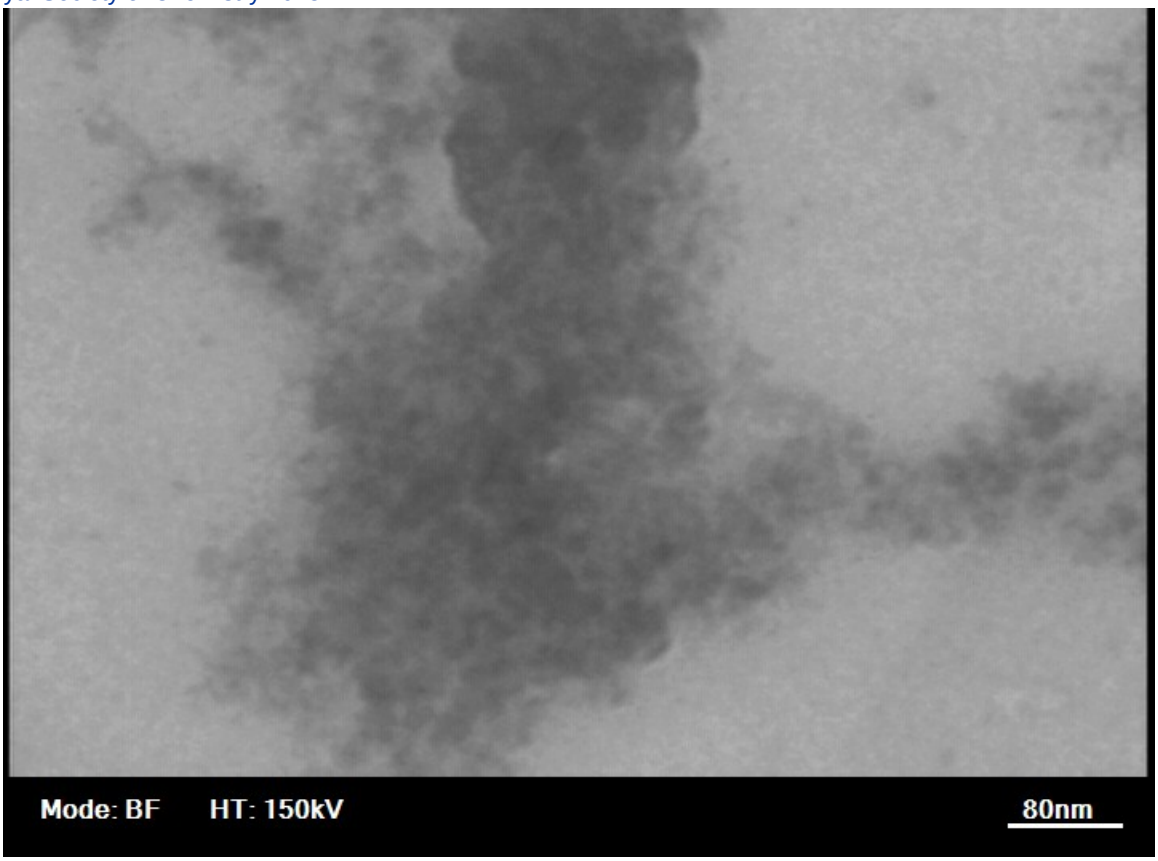

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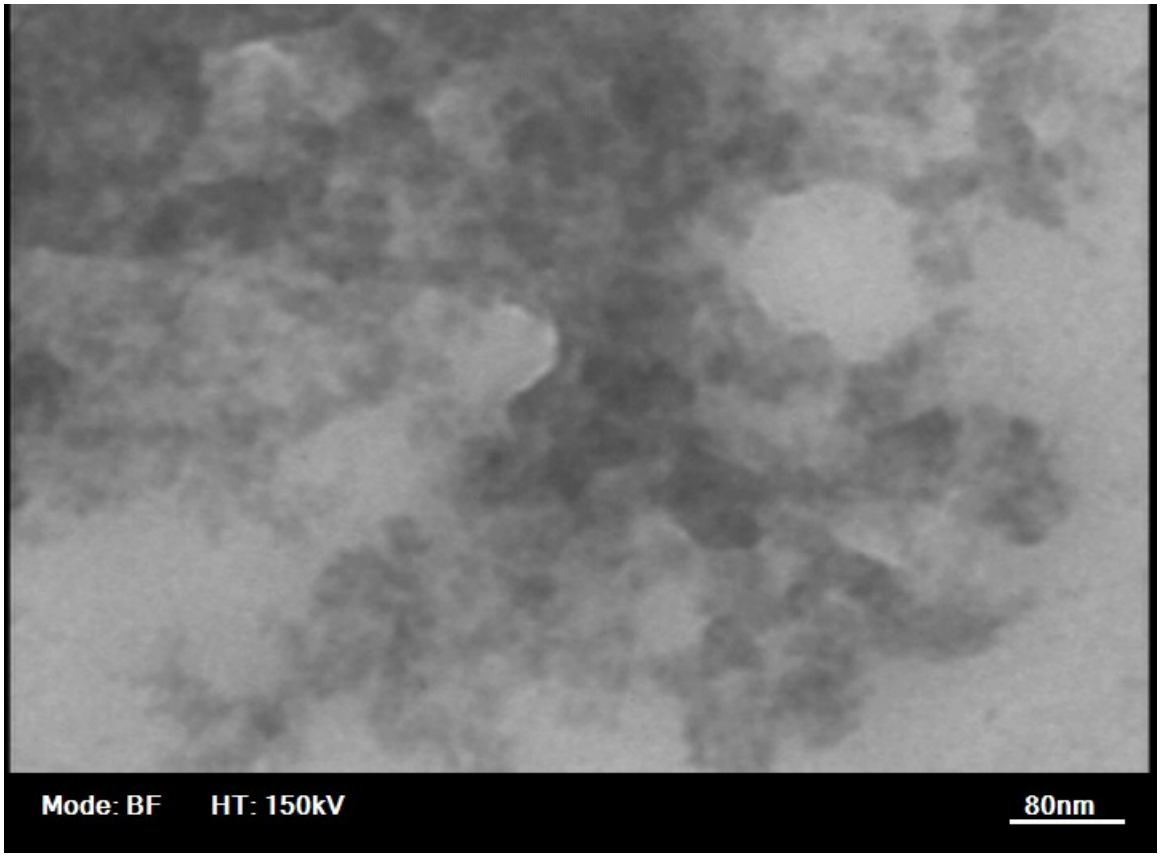

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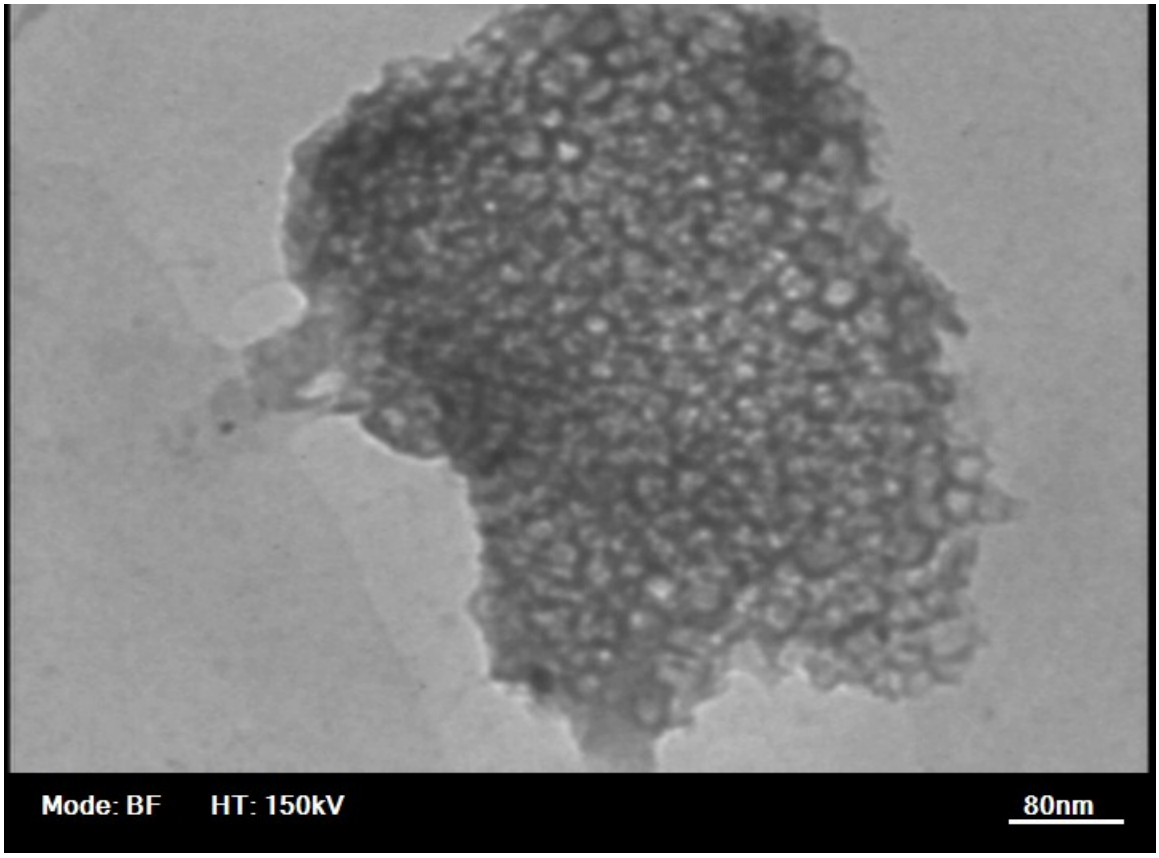
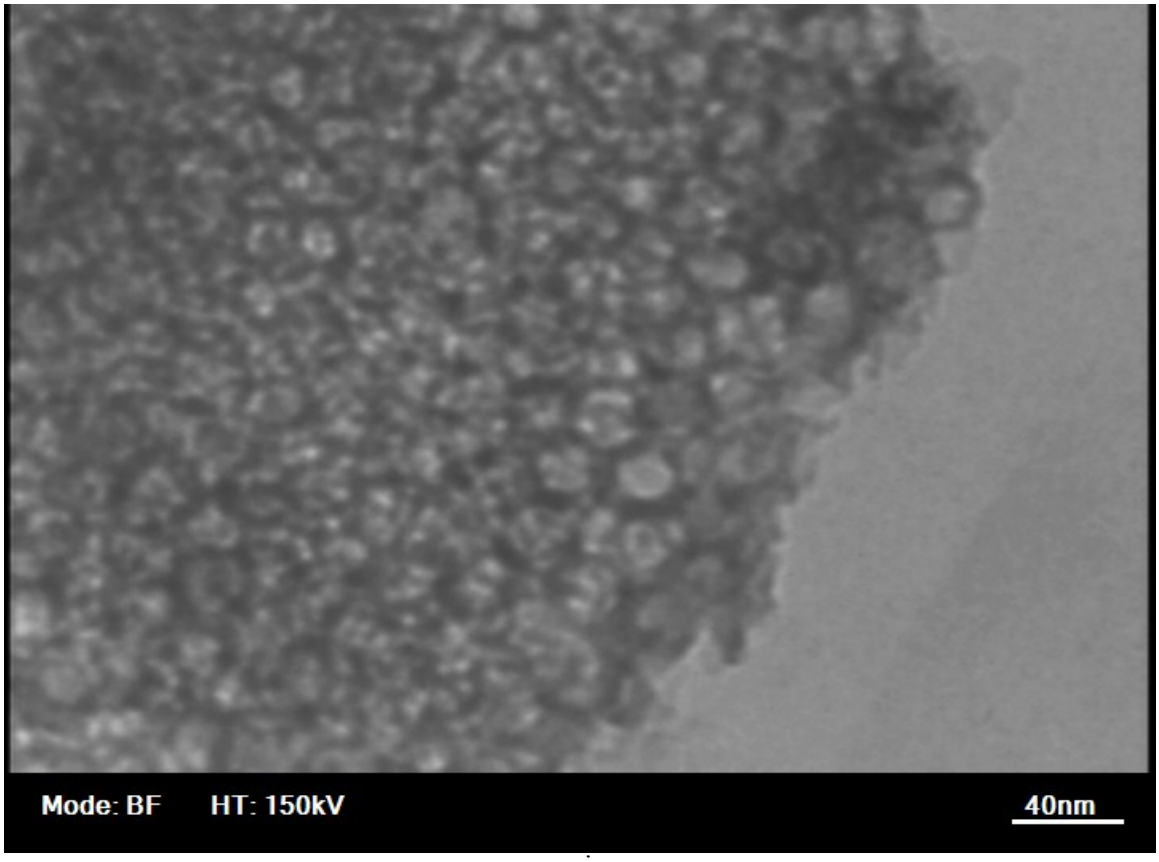


i



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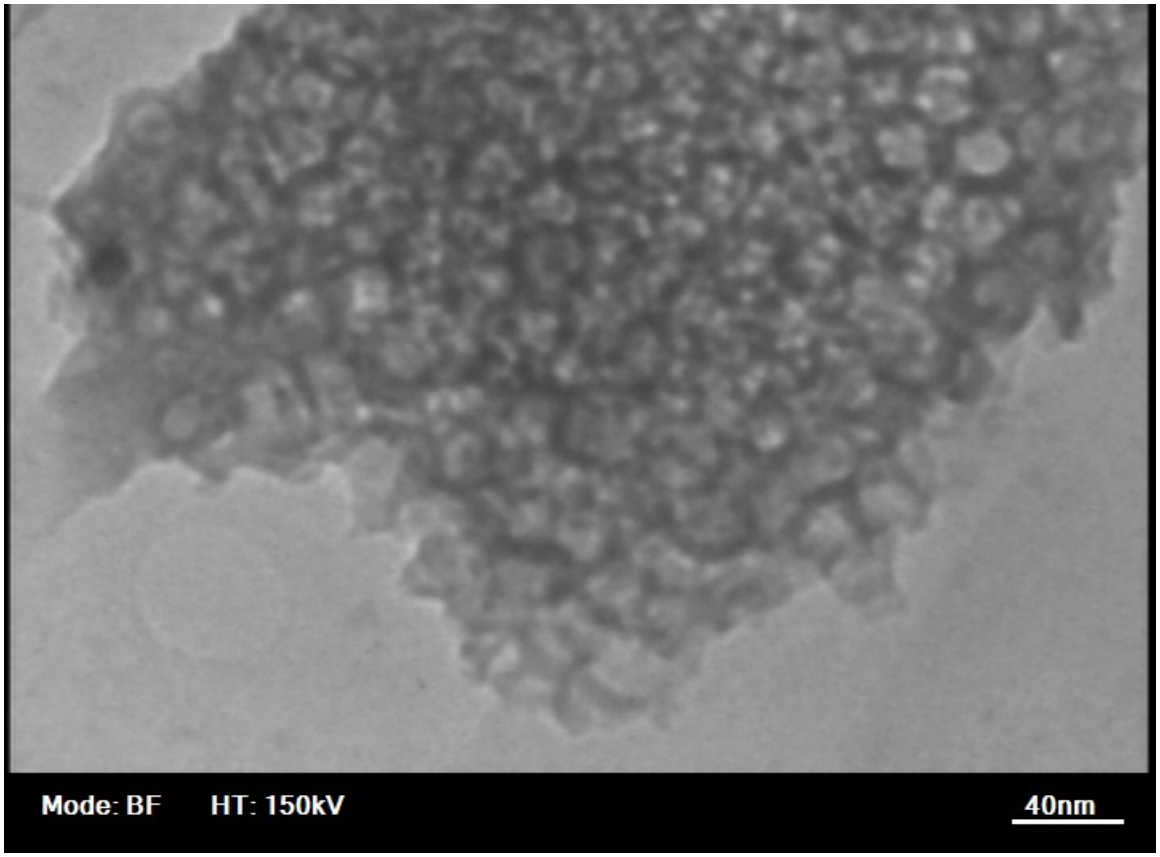


k

Fig. S4 SEM images of l-MnO_x-PVP (a-k).

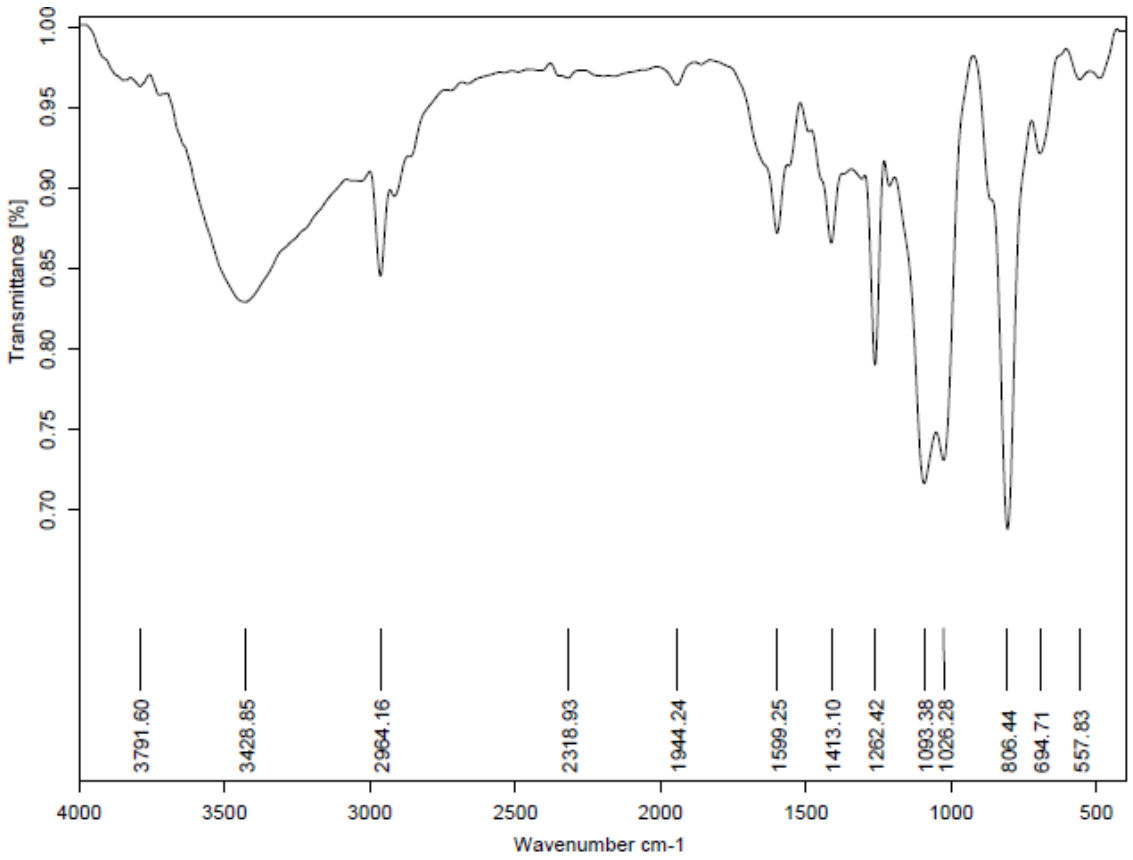


Fig. S5 IR spectrum of PVP.

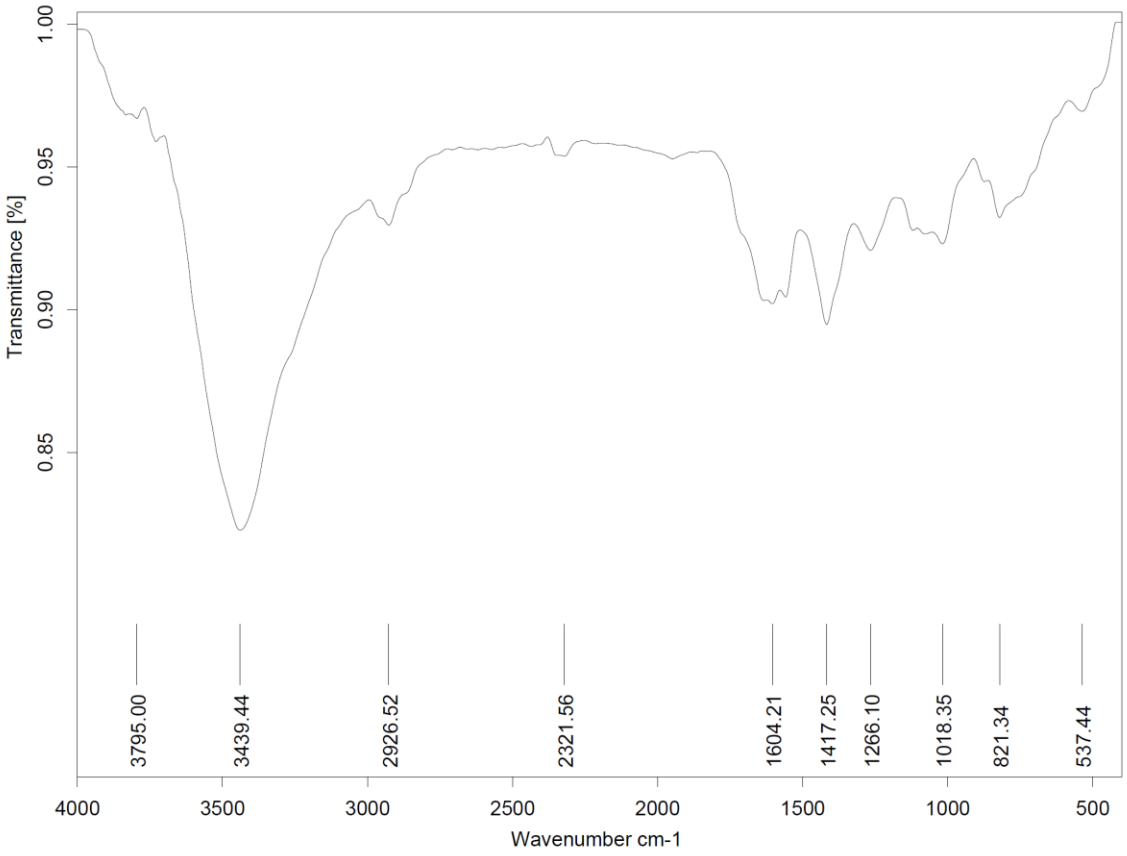


Fig. S6 IR spectrum of l-MnO_x-PVP.

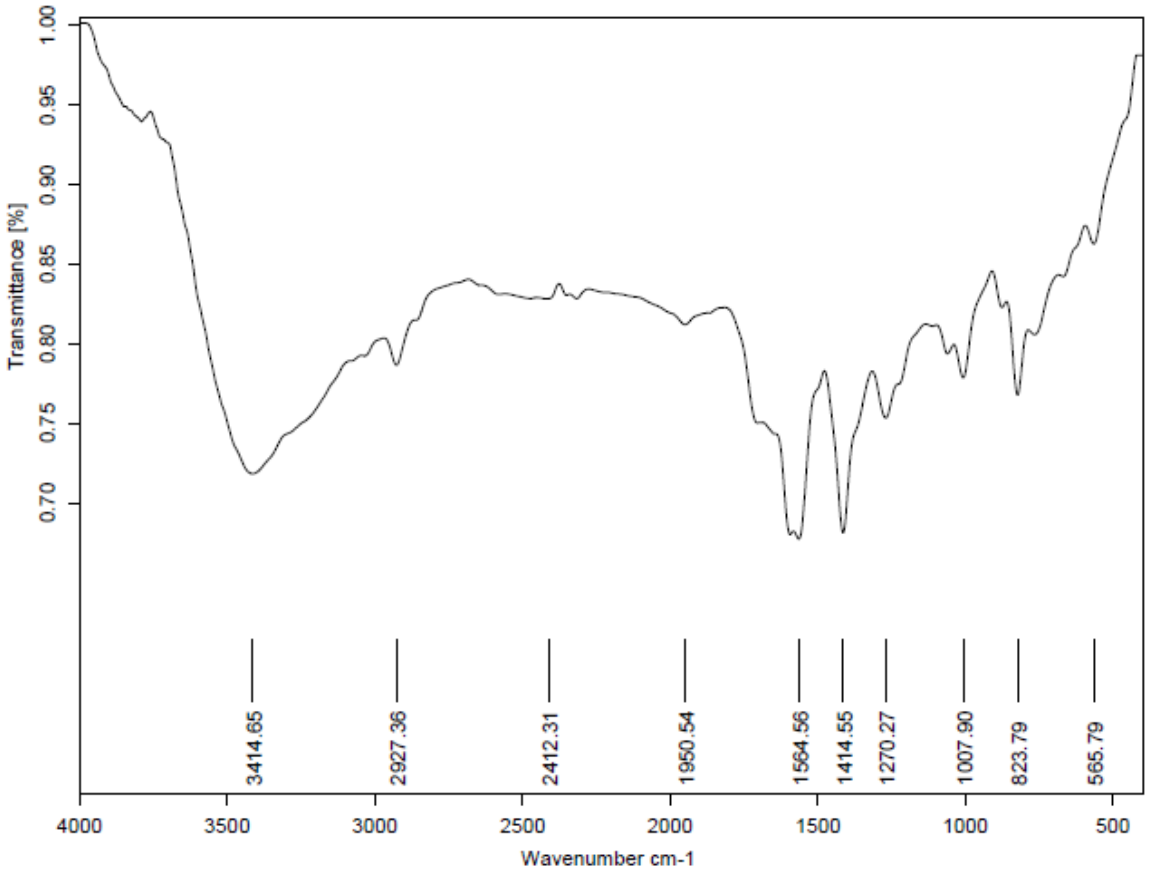


Fig. S7 IR spectrum of m-MnO_x-PVP.

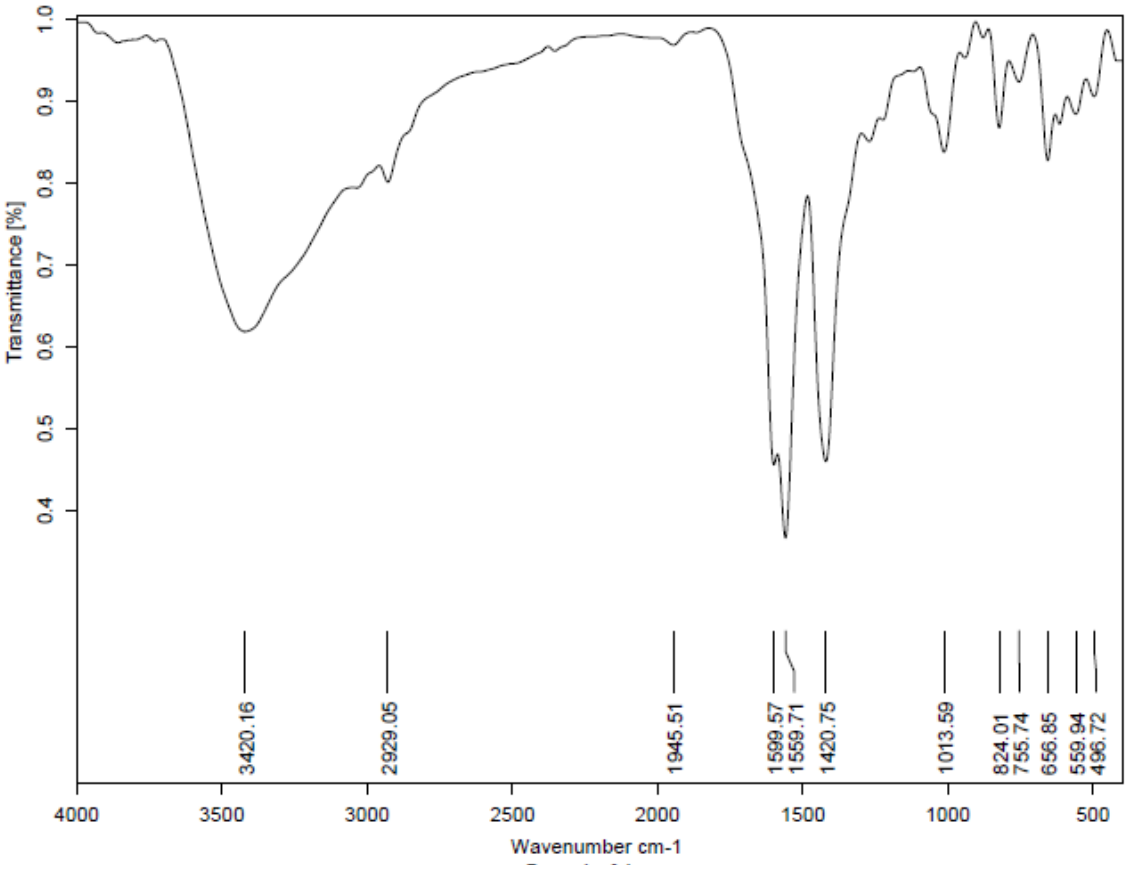


Fig. S8 IR spectrum of h-MnO_x-PVP.

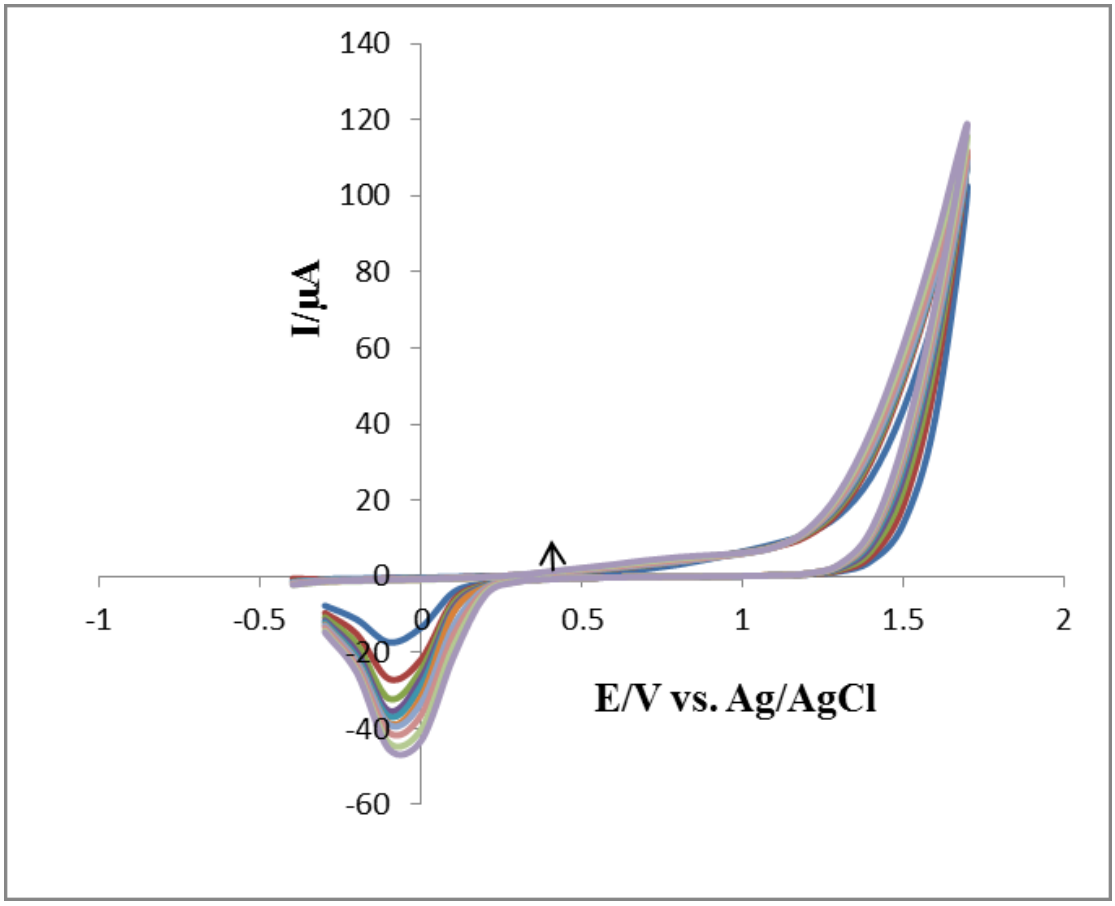


Fig. S9 Cyclic voltammograms of PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

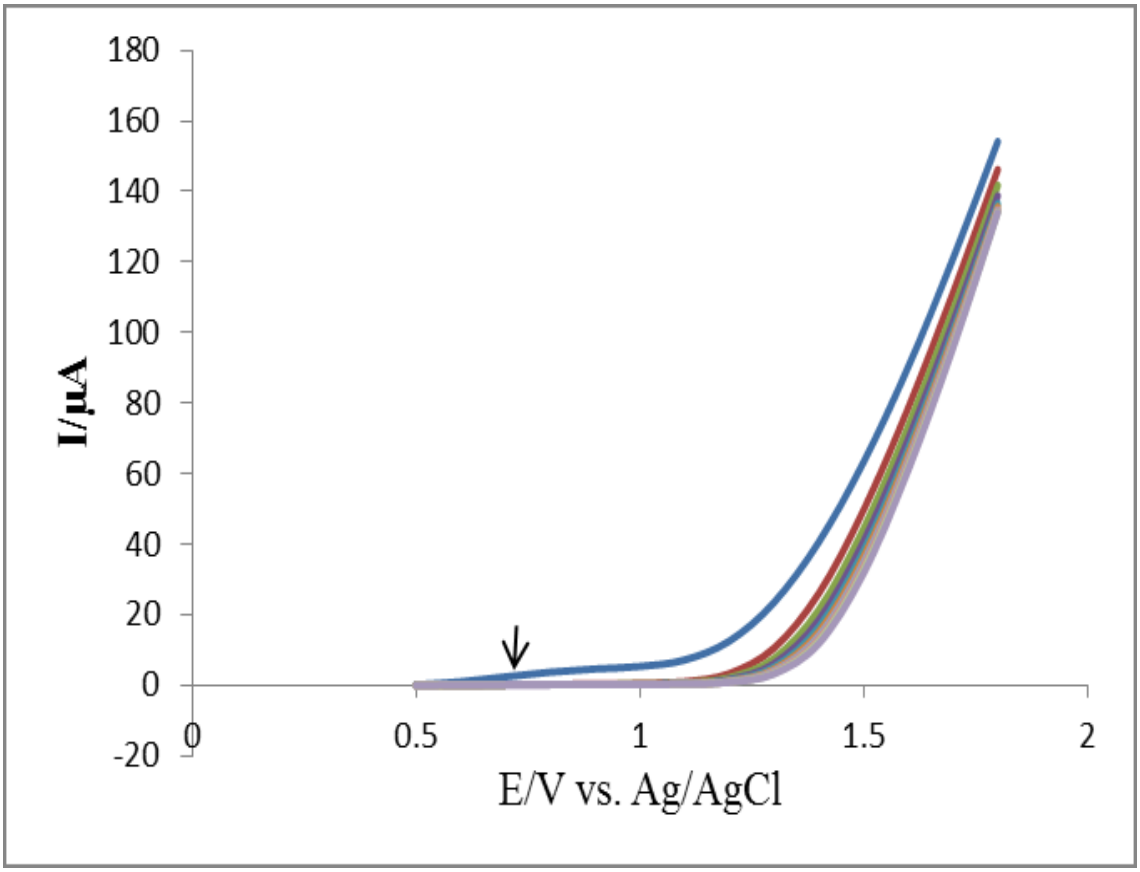


Fig. S10 Linear sweep voltammetry of PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

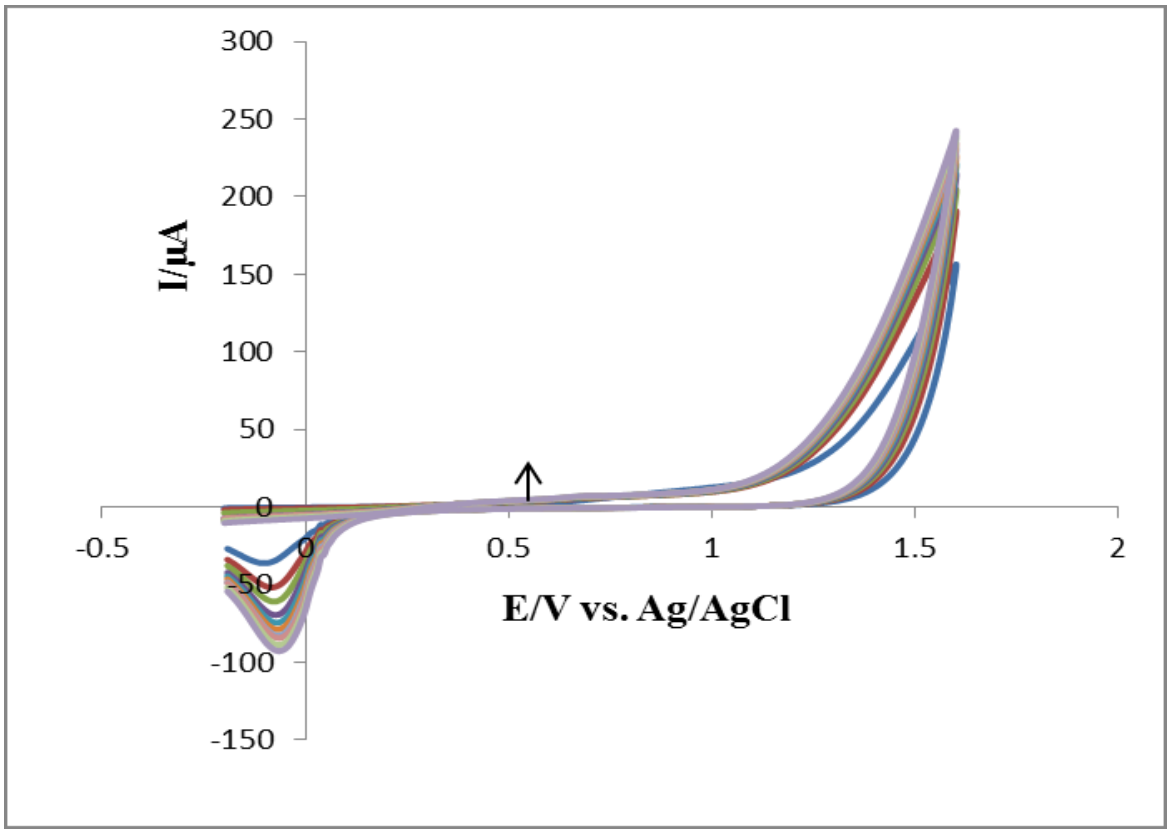


Fig. S11 Cyclic voltammograms of l-MnO_x-PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

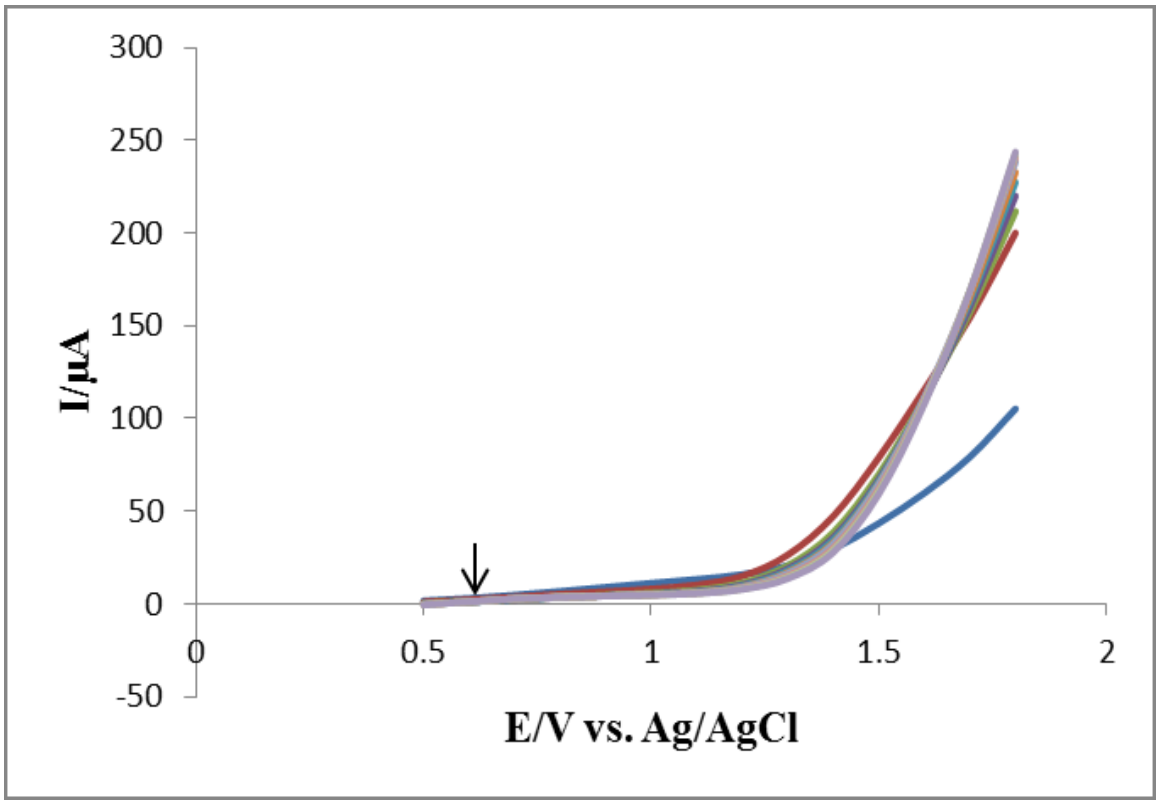


Fig. S12 Linear sweep voltammetry of l-MnO_x-PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

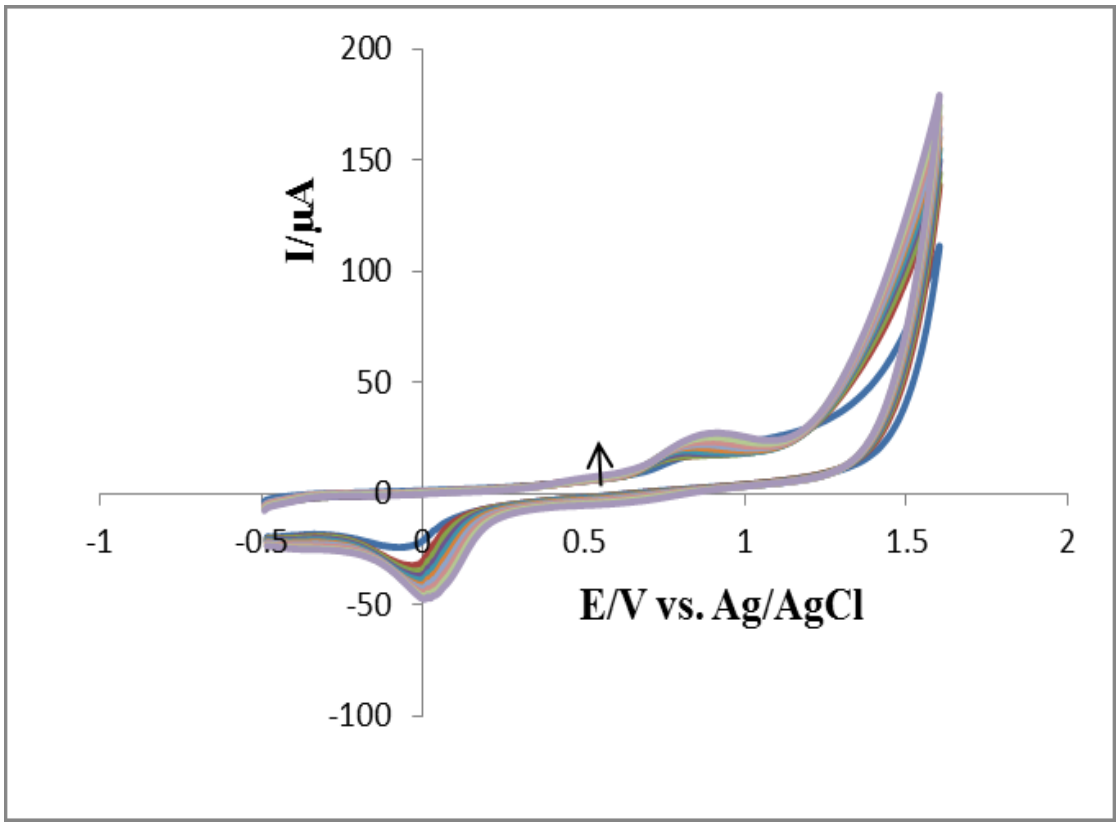


Fig. S13 Cyclic voltammograms of m-MnO_x-PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

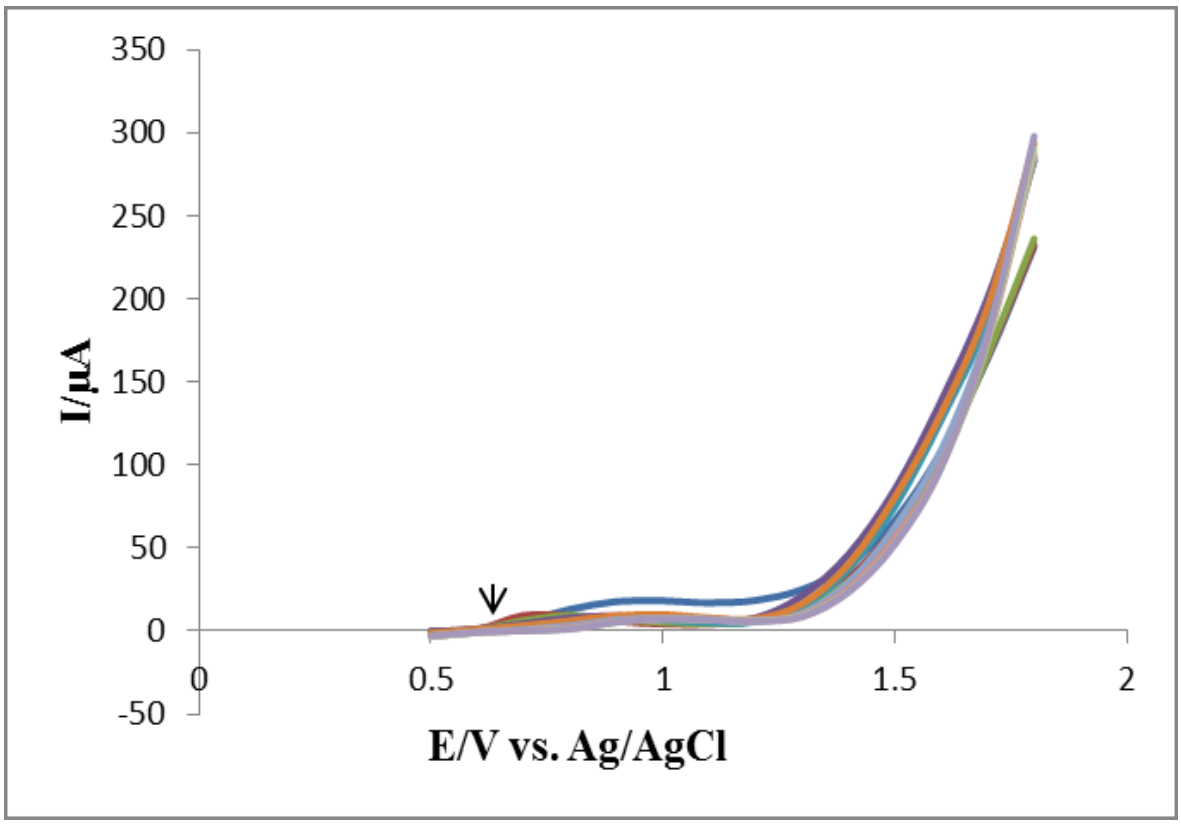


Fig. S14 Linear sweep voltammetry of m-MnO_x-PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

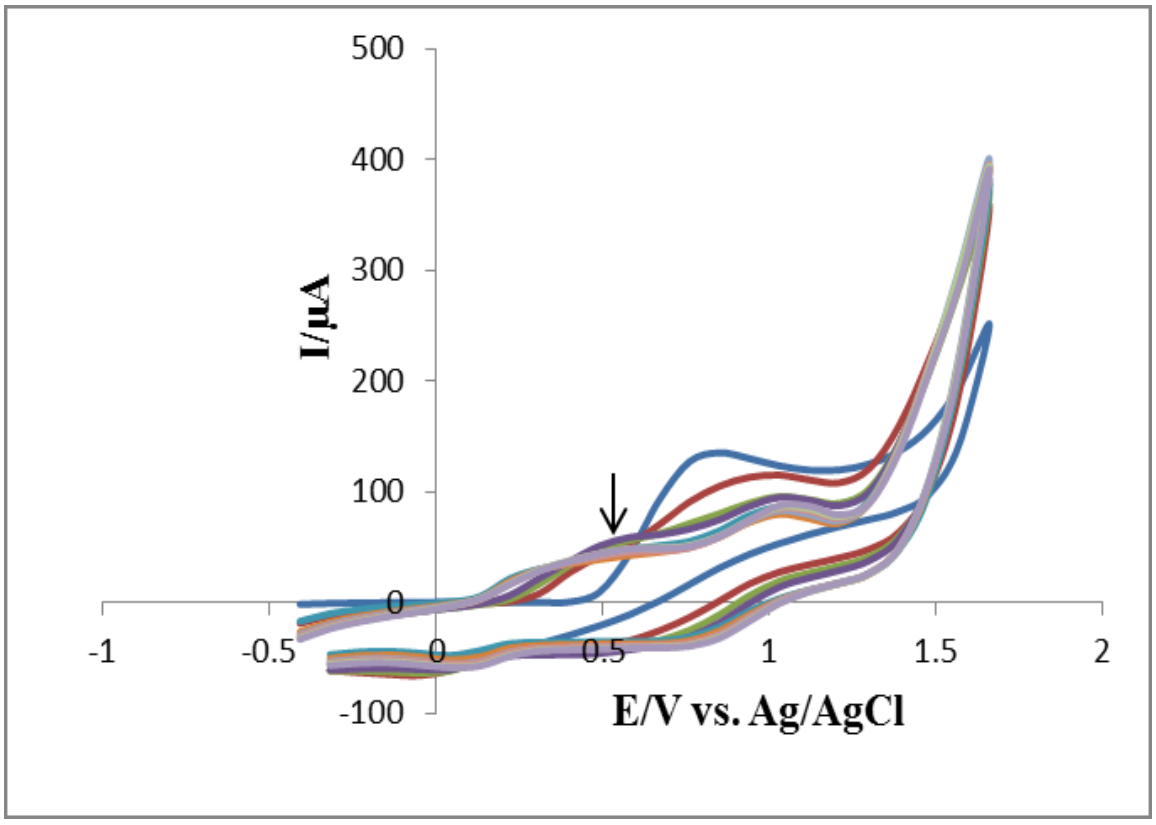


Fig. S15 Cyclic voltammograms of h-MnO_x-PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

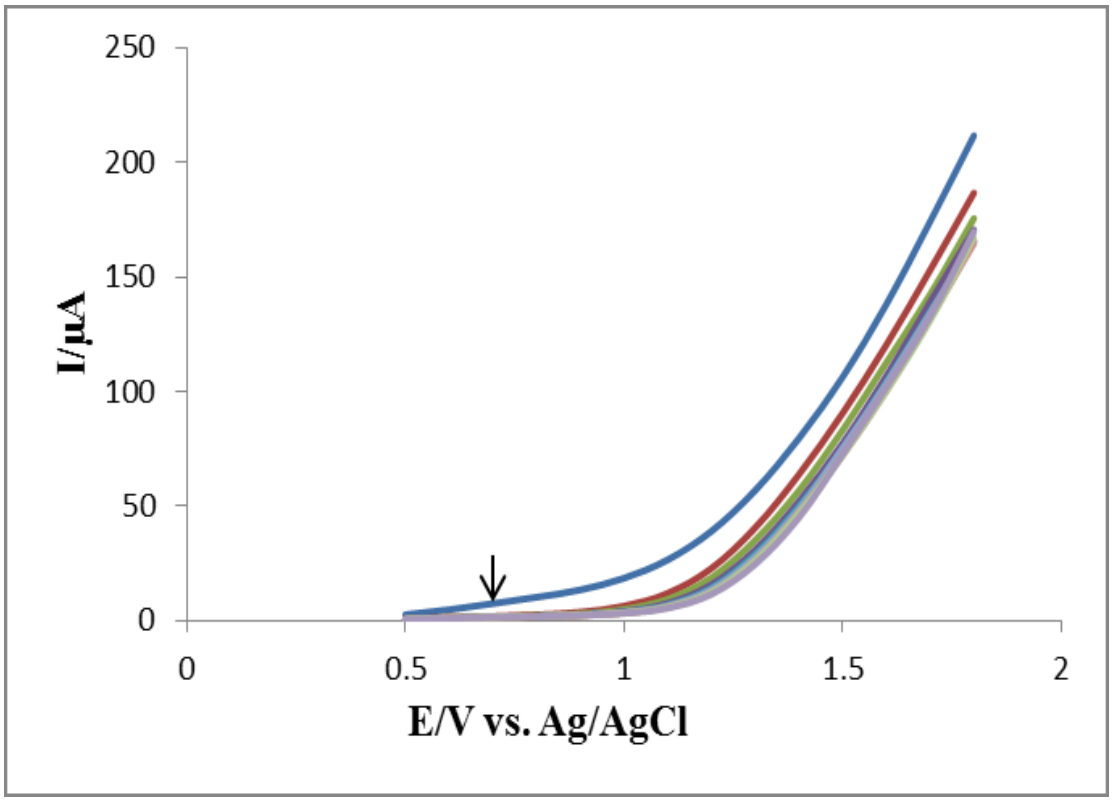


Fig. S16 Linear sweep voltammetry of h-MnO_x-PVP in lithium perchlorate solution (0.1 M in water, pH = 6.3) at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

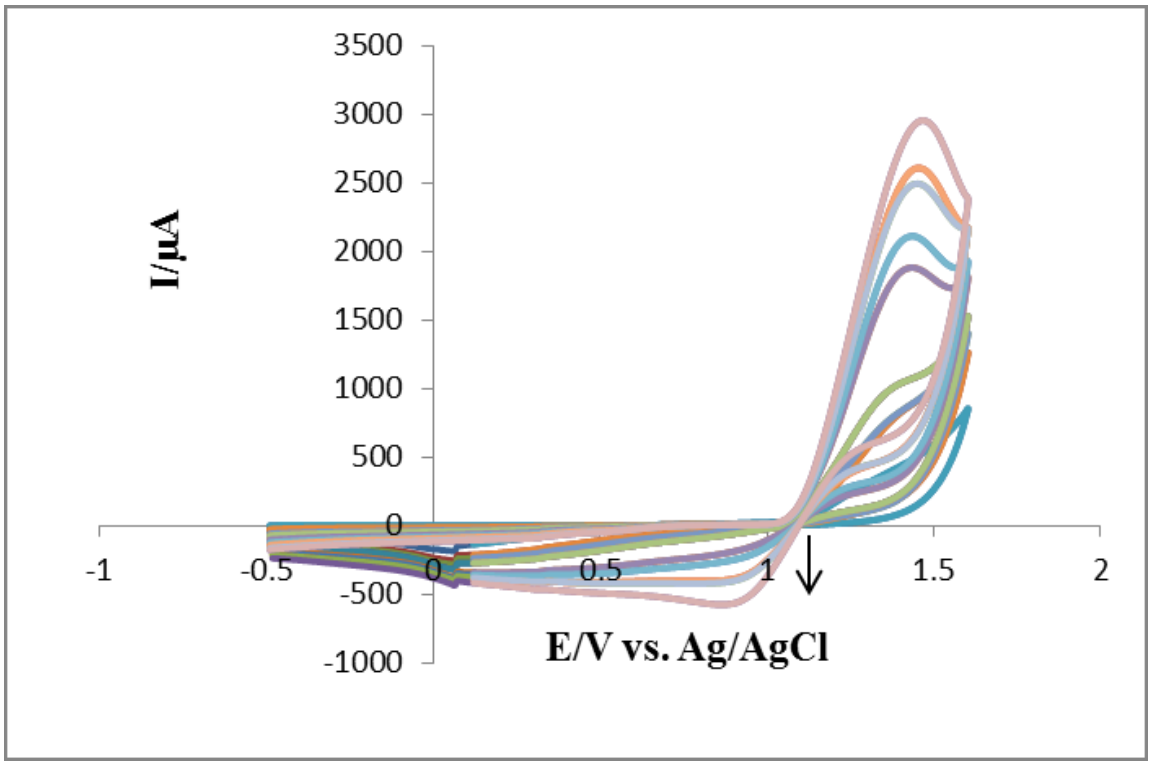


Fig. S17 Cyclic voltammograms of l-MnO_x-PVP in Persian Gulf water at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

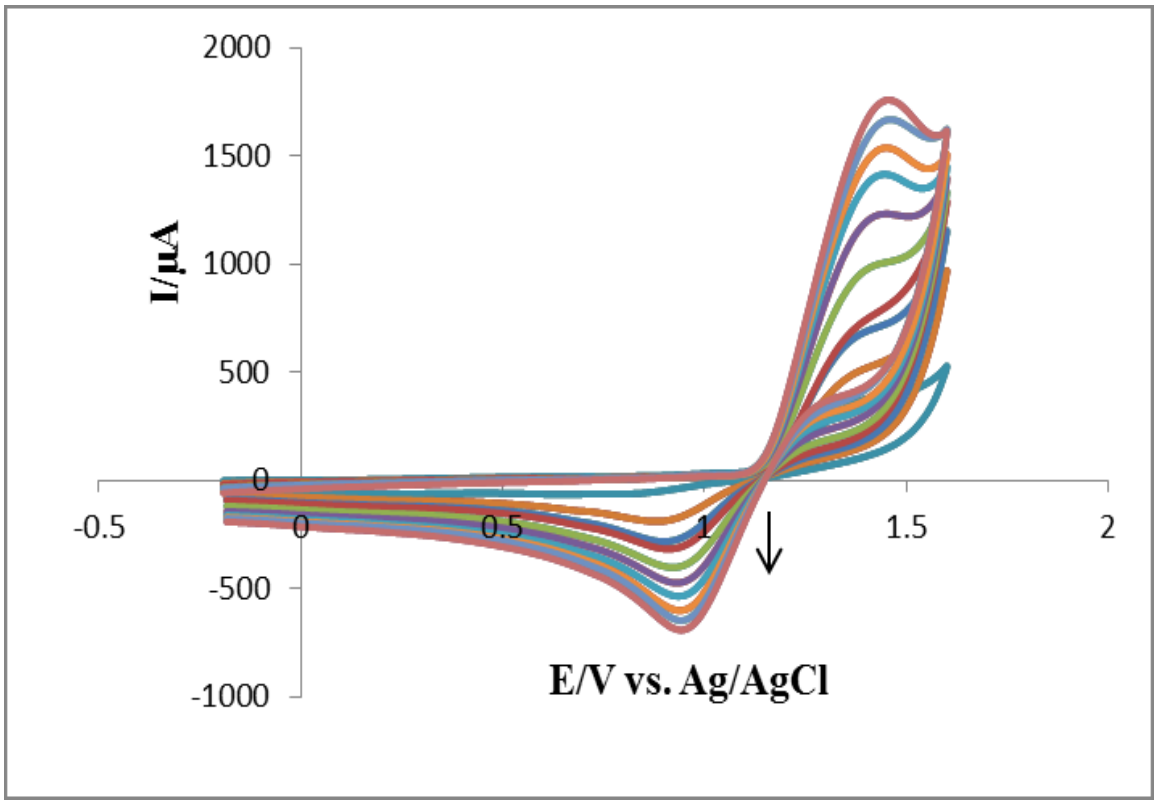


Fig. S18 Cyclic voltammograms Persian Gulf water at a scan rate of 100 mV s^{-1}. The different colors correspond to different cycles on the same electrode.

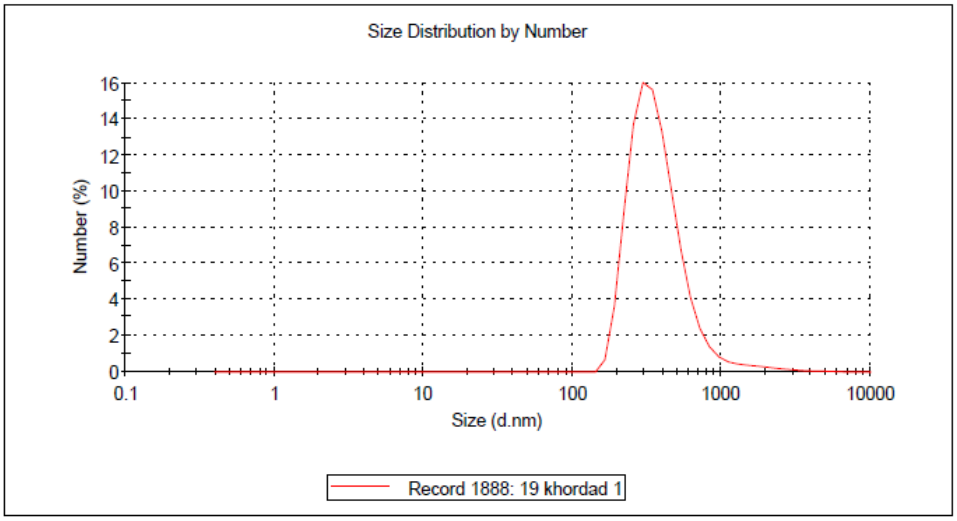
System

Temperature (°C):	25.0	**Duration Used (s):**	70
Count Rate (kcps):	182.6	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	6

Results

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	722.8	**Peak 1:**	463.5	50.7	182.0
PdI:	0.533	**Peak 2:**	2461	42.9	1102
Intercept:	0.821	**Peak 3:**	5191	6.4	379.3

Result quality : Good



a

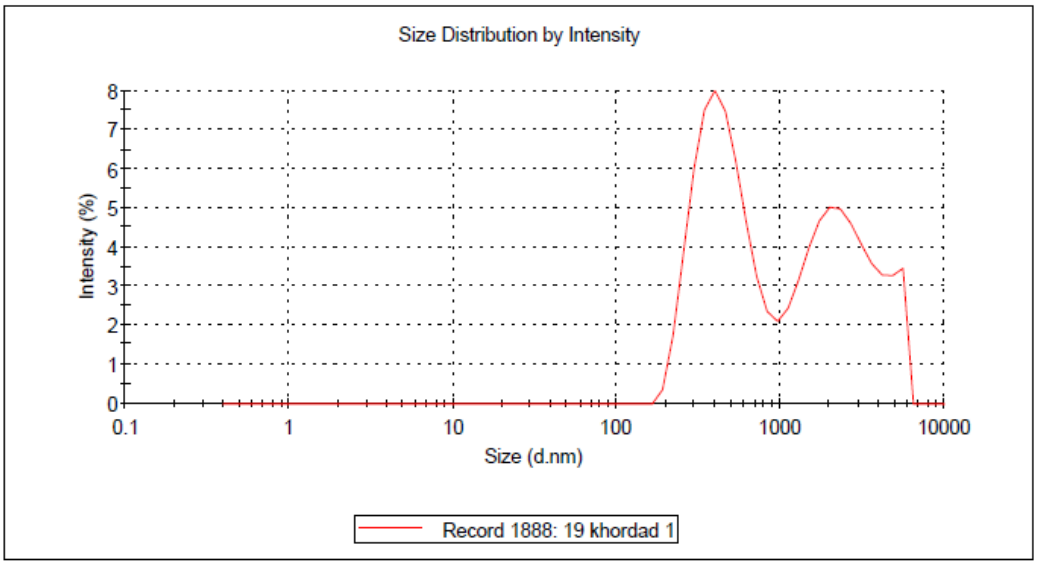
System

Temperature (°C):	25.0	**Duration Used (s):**	70
Count Rate (kcps):	182.6	**Measurement Position (mm):**	4.65
Cell Description:	Disposable sizing cuvette	**Attenuator:**	6

Results

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	722.8	**Peak 1:**	463.5	50.7	182.0
PdI:	0.533	**Peak 2:**	2461	42.9	1102
Intercept:	0.821	**Peak 3:**	5191	6.4	379.3

Result quality : Good



b

Size d.nm	Mean Number %	Std Dev Number %
0.4000	0.0	
0.4632	0.0	
0.5365	0.0	
0.6213	0.0	
0.7195	0.0	
0.8332	0.0	
0.9649	0.0	
1.117	0.0	
1.294	0.0	
1.499	0.0	
1.736	0.0	
2.010	0.0	
2.328	0.0	
2.696	0.0	
3.122	0.0	
3.615	0.0	
4.187	0.0	
4.849	0.0	

Size d.nm	Mean Number %	Std Dev Number %
5.615	0.0	
6.503	0.0	
7.531	0.0	
8.721	0.0	
10.10	0.0	
11.70	0.0	
13.54	0.0	
15.69	0.0	
18.17	0.0	
21.04	0.0	
24.36	0.0	
28.21	0.0	
32.67	0.0	
37.84	0.0	
43.82	0.0	
50.75	0.0	
58.77	0.0	
68.06	0.0	

Size d.nm	Mean Number %	Std Dev Number %
78.82	0.0	
91.28	0.0	
105.7	0.0	
122.4	0.0	
141.8	0.0	
164.2	0.7	
190.1	3.6	
220.2	8.8	
255.0	13.7	
295.3	16.0	
342.0	15.6	
396.1	13.3	
458.7	10.0	
531.2	6.7	
615.1	4.1	
712.4	2.4	
825.0	1.4	
955.4	0.8	

Size d.nm	Mean Number %	Std Dev Number %
1106	0.6	
1281	0.4	
1484	0.4	
1718	0.3	
1990	0.3	
2305	0.2	
2669	0.2	
3091	0.1	
3580	0.1	
4145	0.1	
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7456	0.0	
8635	0.0	
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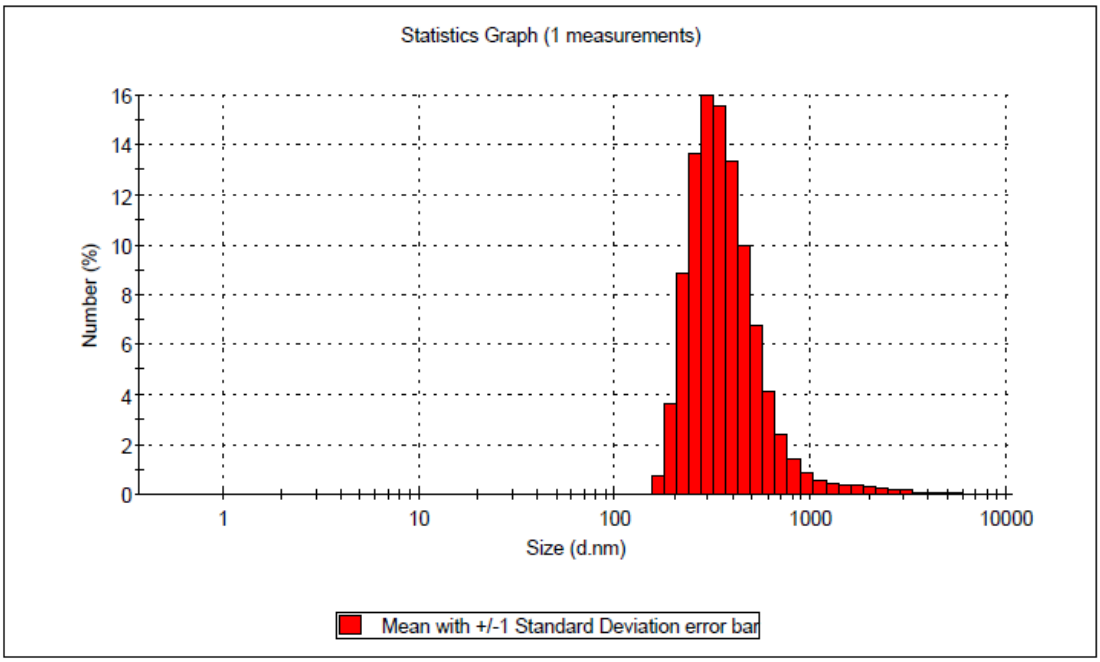


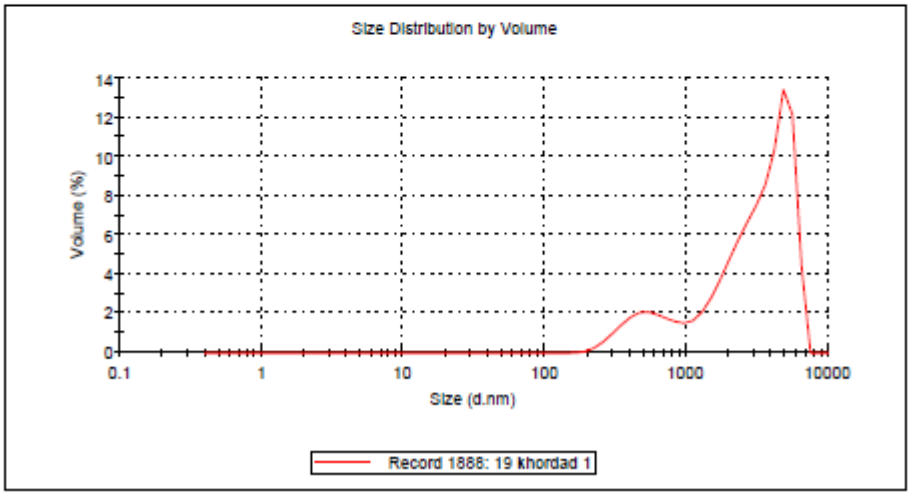
c

System

Temperature (°C):	25.0	Duration Used (s):	70
Count Rate (kcps):	182.6	Measurement Position (mm):	4.65
Cell Description:	Disposable sizing cuvette	Attenuator:	6

Results

			Diam. (nm)	% Intensity	Width (nm)
Z-Average (d.nm):	722.8	Peak 1:	463.5	50.7	182.0
PdI:	0.533	Peak 2:	2461	42.9	1102
Intercept:	0.821	Peak 3:	5191	6.4	379.3
Result quality :	Good				



d

Fig. S19 Details for DLS experiments (a-d).

References

1 Y. Umena, K. Kawakami, J. R. Shen and N. Kamiya, *Nature*, 2011, **473**, 55.