Electronic Supplementary Information

A very simple and high-yield method to synthesize nanolayered Mn oxide†

Mohammad Mahdi Najafpour[a,b,*] and Emad Amini[a]

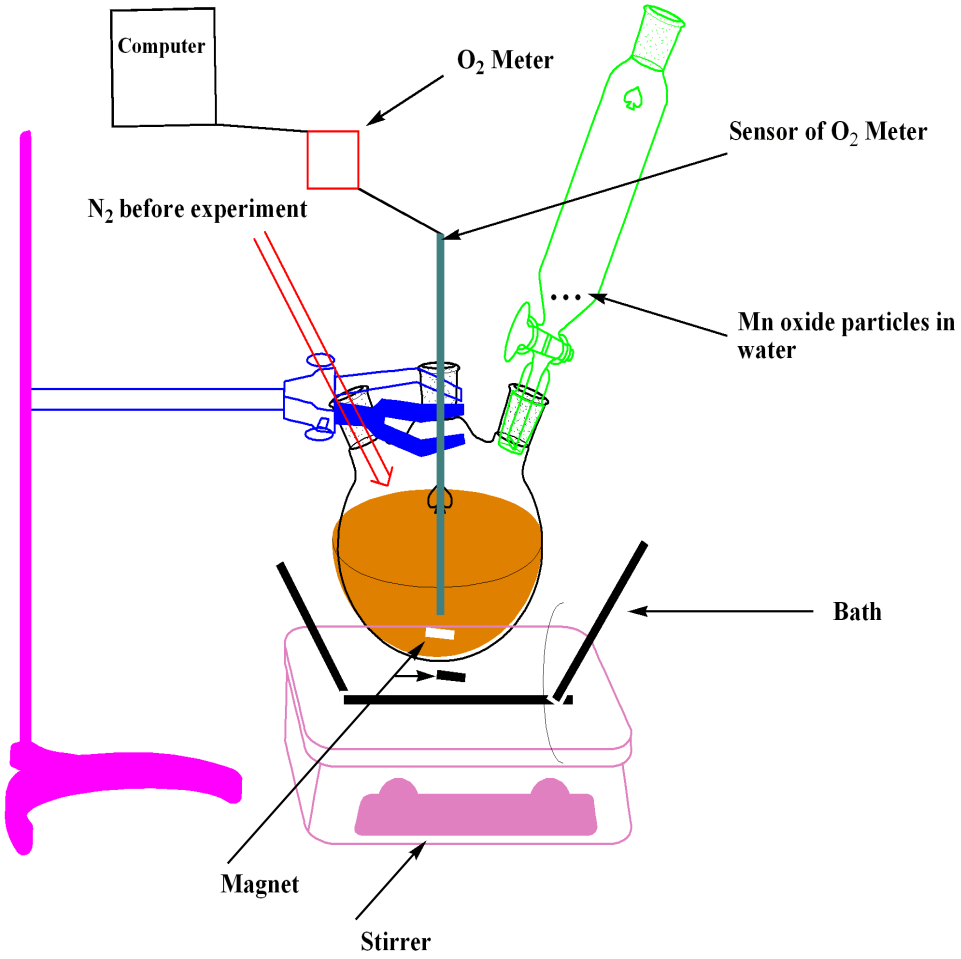
[a] Department of Chemistry, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran
[b] Center of Climate Change and Global Warming, Institute for Advanced Studies in Basic Sciences (IASBS), Zanjan, 45137-66731, Iran
Corresponding author; Phone: (+98) 241 415 3201; E-mail: mmnajafpour@iasbs.ac.ir (MMN);

Contents

Title	Page
The reactor set-up	4
FTIR spectra	5
TEM and HRTEM	6
SEM images	10
XRD spectra	19

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, Mn oxides as several small particles were added, and oxygen evolution was recorded with the oxygen meter under stirring (Scheme S1). 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.



Scheme S1. The reactor set-up for oxygen evolution experiment in the presence of Ce(IV).

Fig. S1 An image from the reaction of soap, KOH, $MnCl_2$ and H_2O_2.

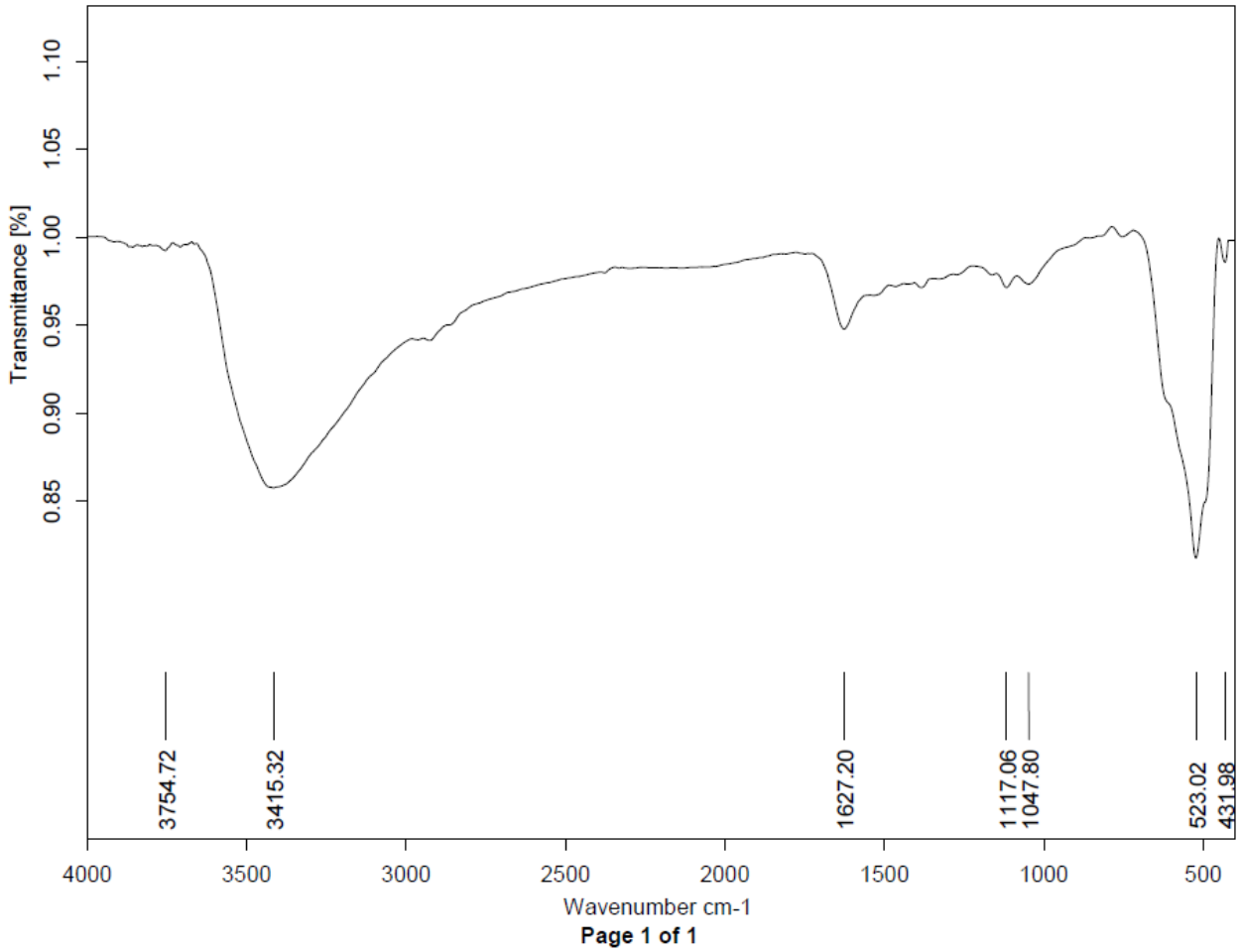
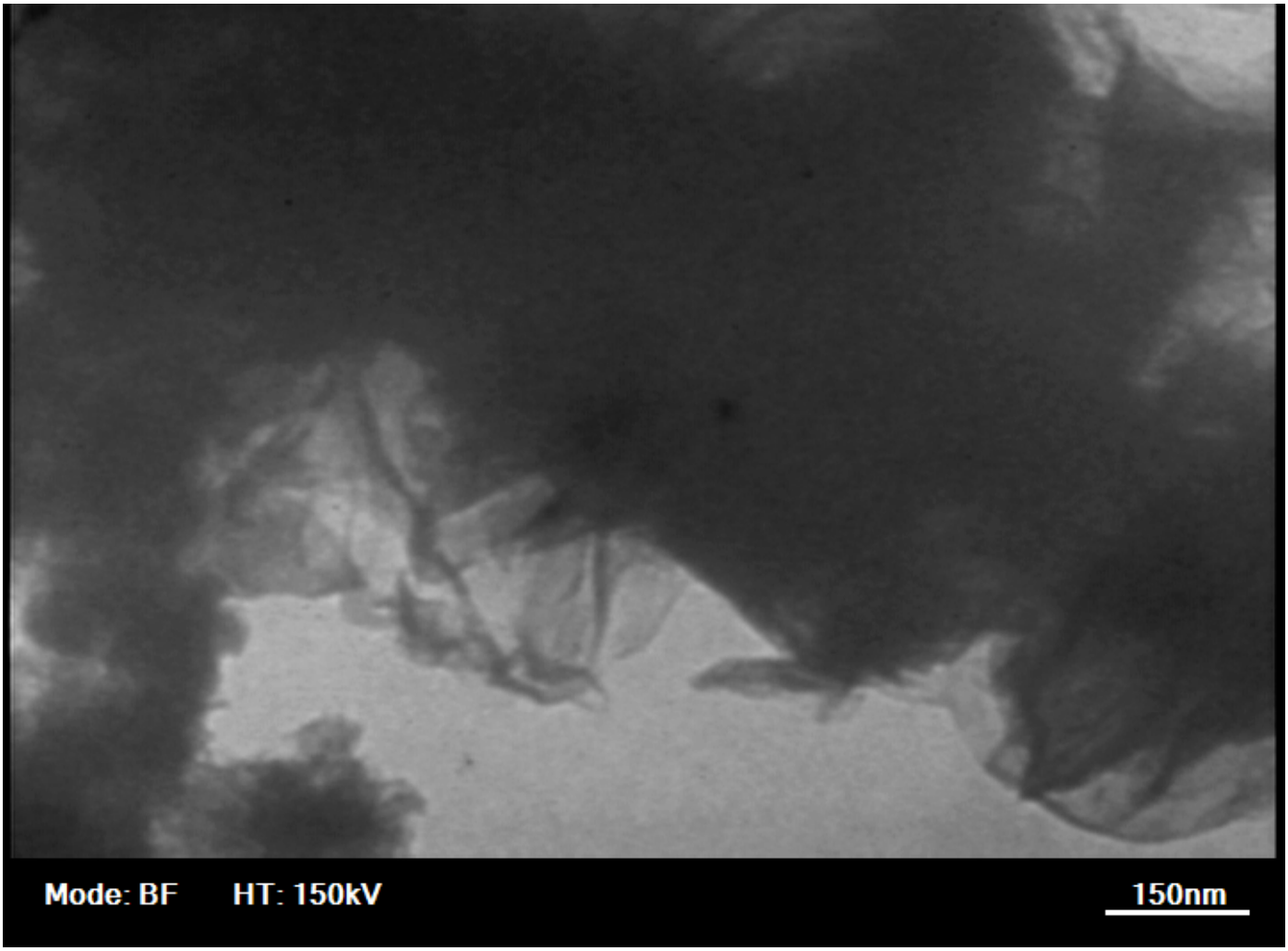
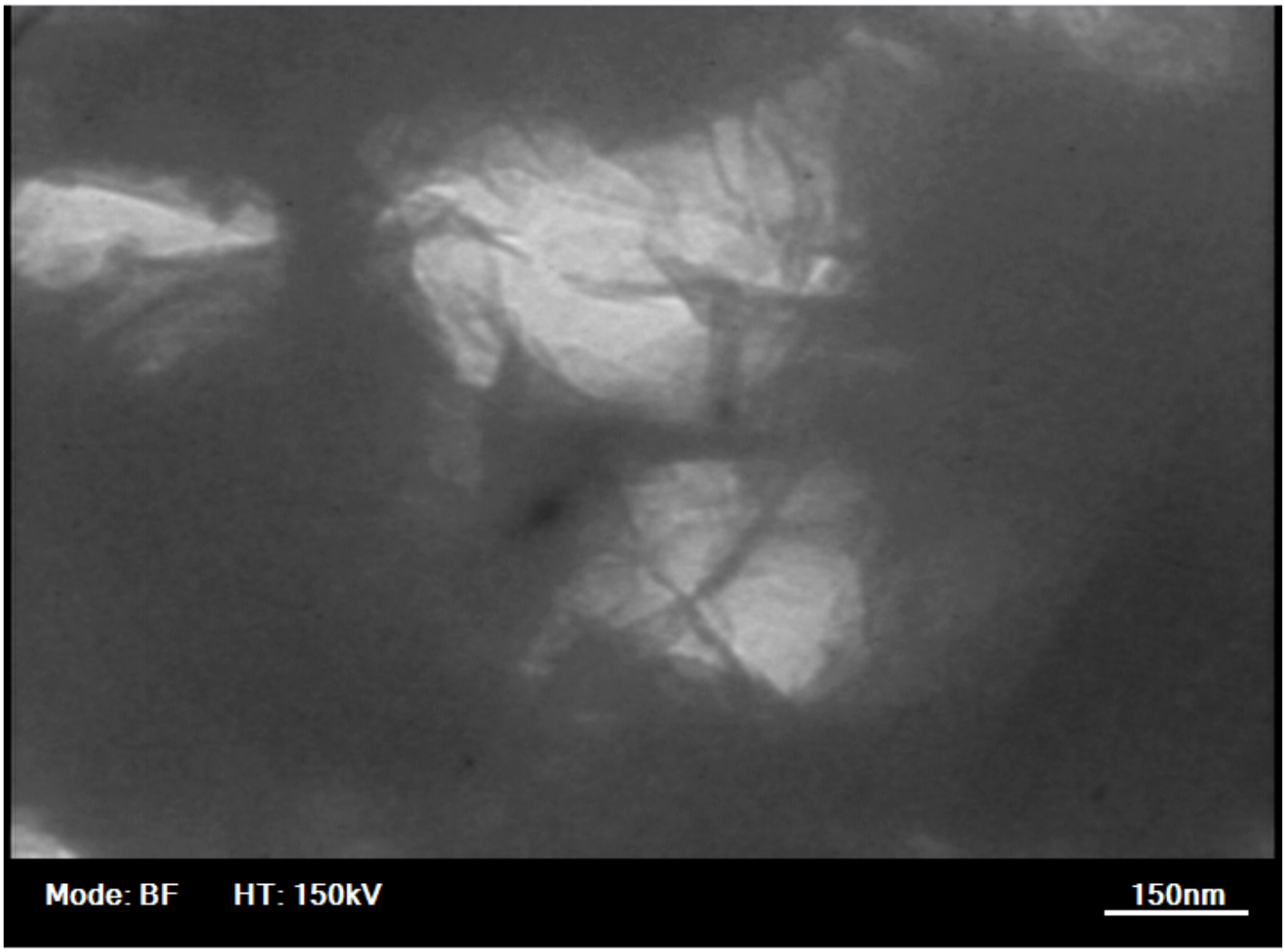


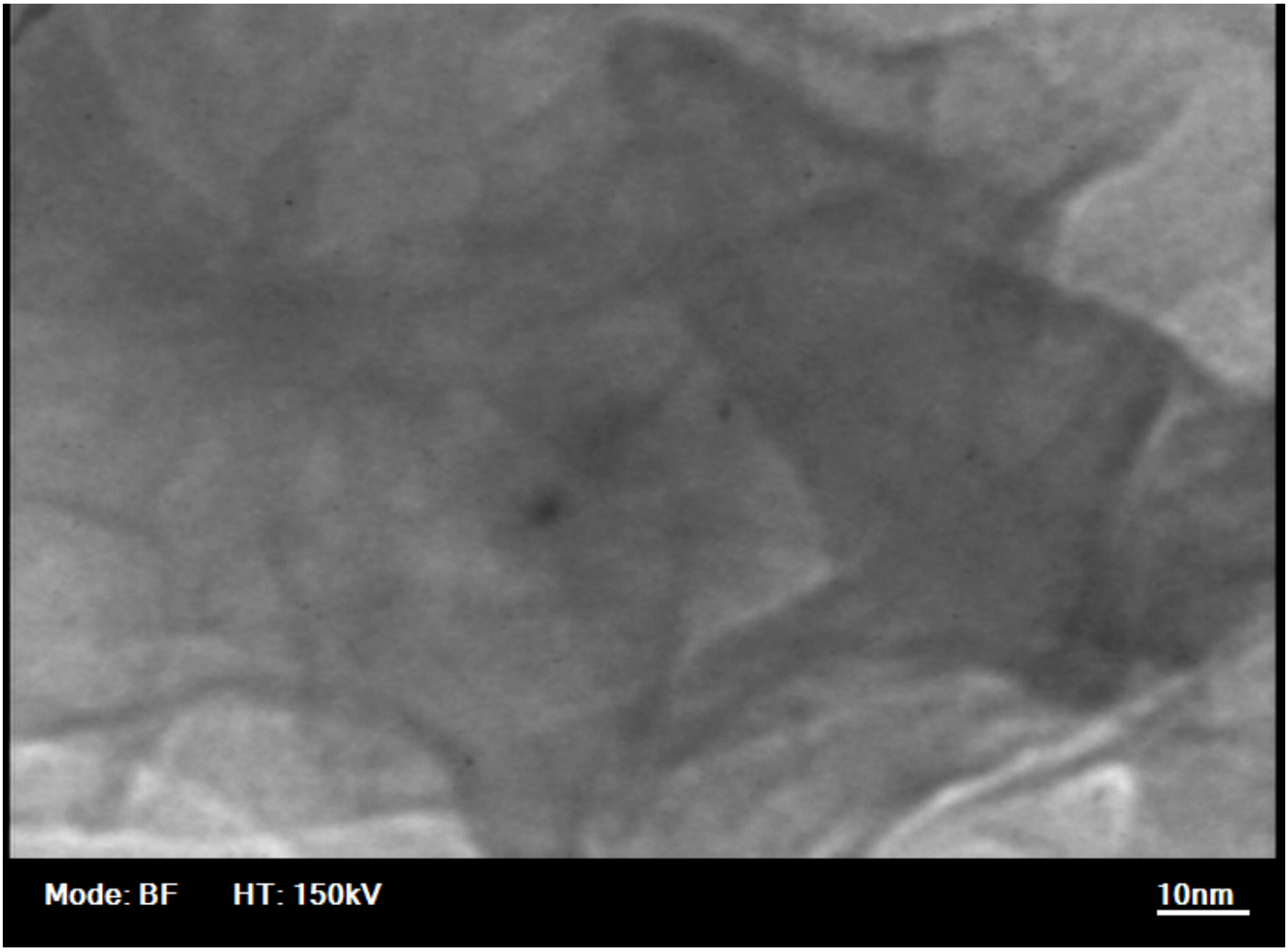
Fig. S2 FTIR from calcined **5** at 300 ^{o}C. a broad band at ~ 3200-3500 cm^{-1} related to antisymmetric and symmetric O-H stretchings and at ~ 1630 cm^{-1} related to H-O-H bending are observed. The absorption bands characteristic for a MnO_6 core in the region ~ 520 cm^{-1} assigned to stretching vibrations of Mn-O bonds in Mn oxide.



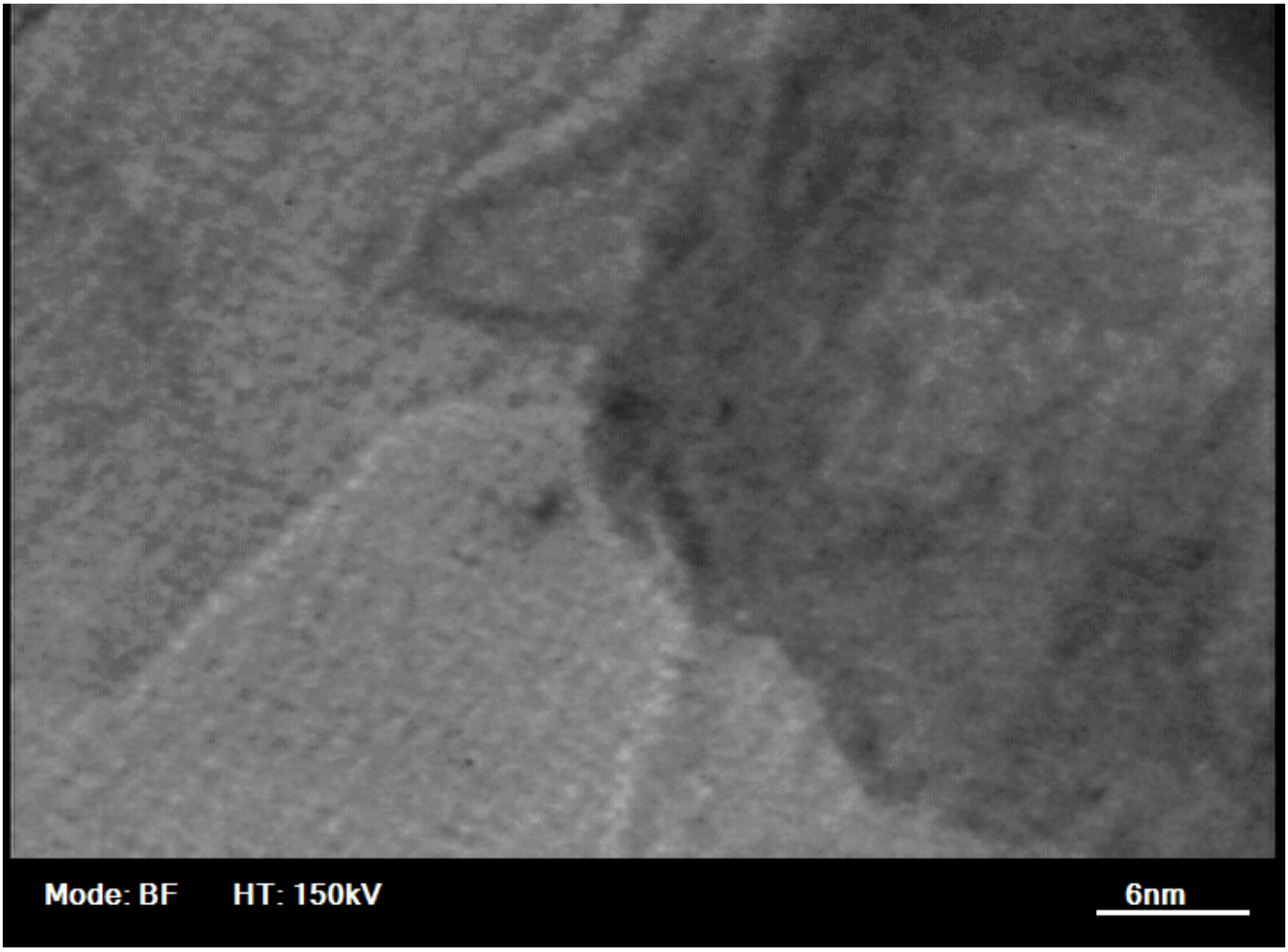
a



b

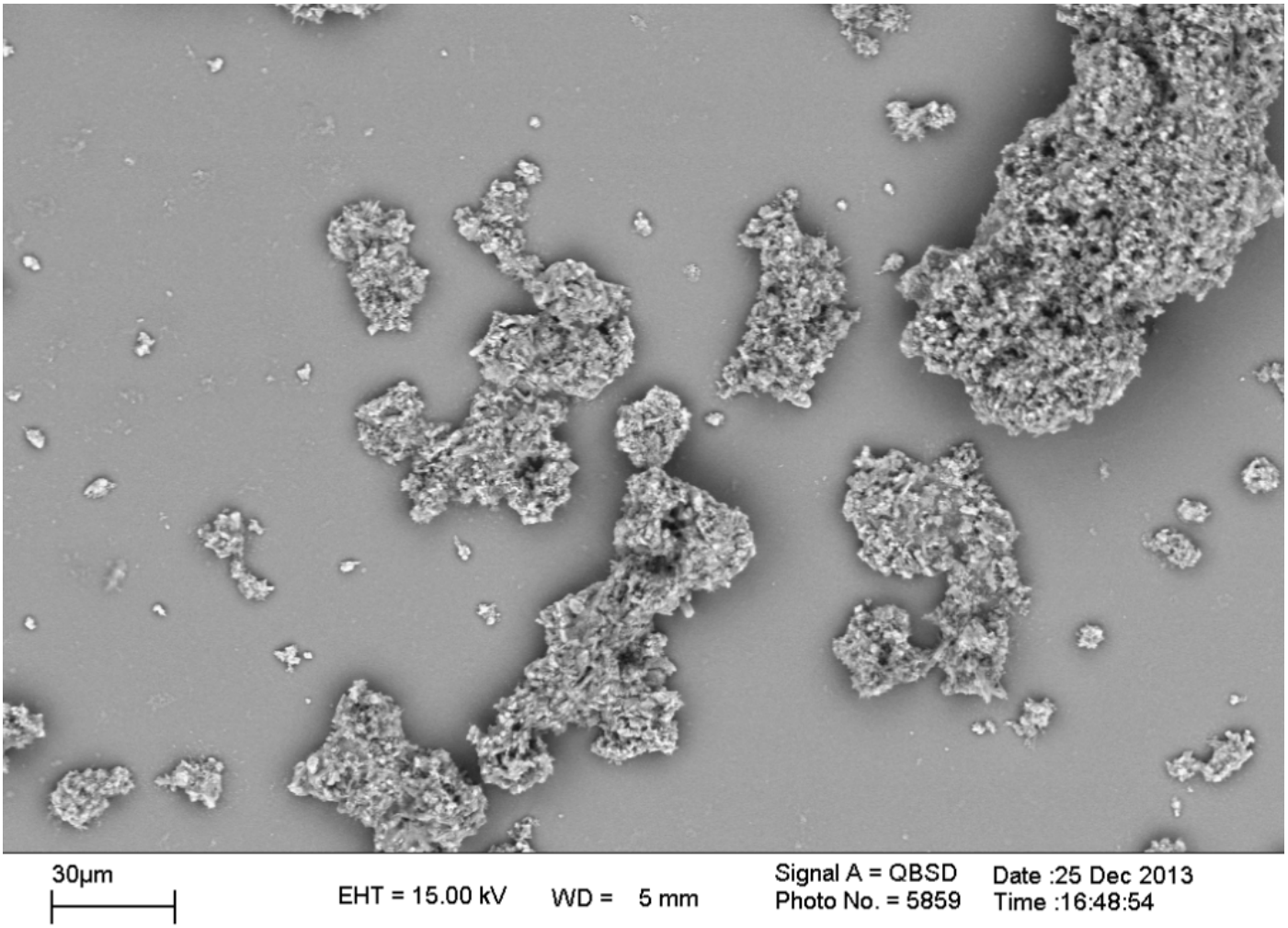


c

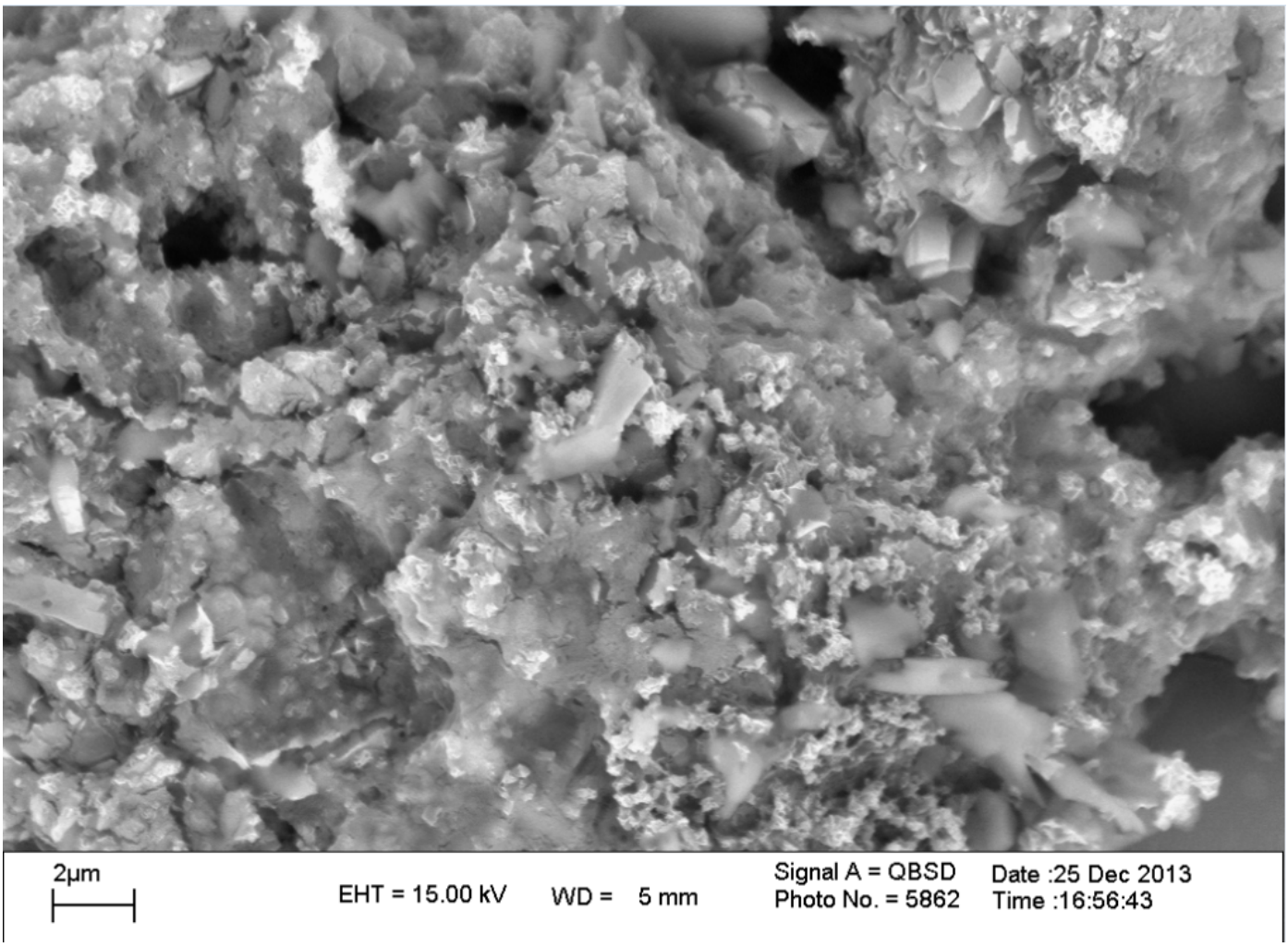


d

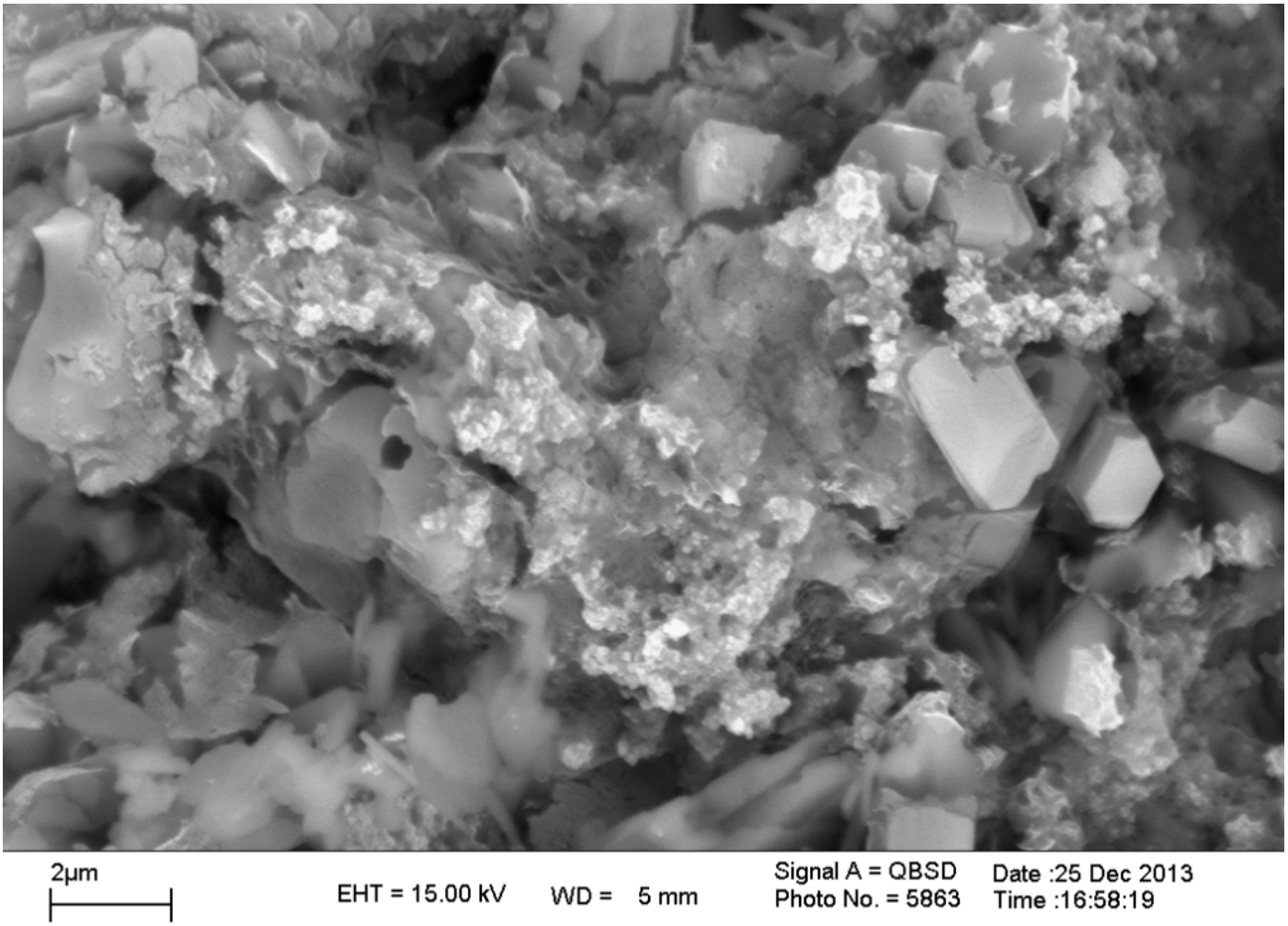
Fig. S3 TEM and HRTEM images of nanolayered Mn oxide for prepared samples in table 1(for **6**) . Images show layers in this compound.


30µm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 5859
Date :25 Dec 2013
Time :16:48:54

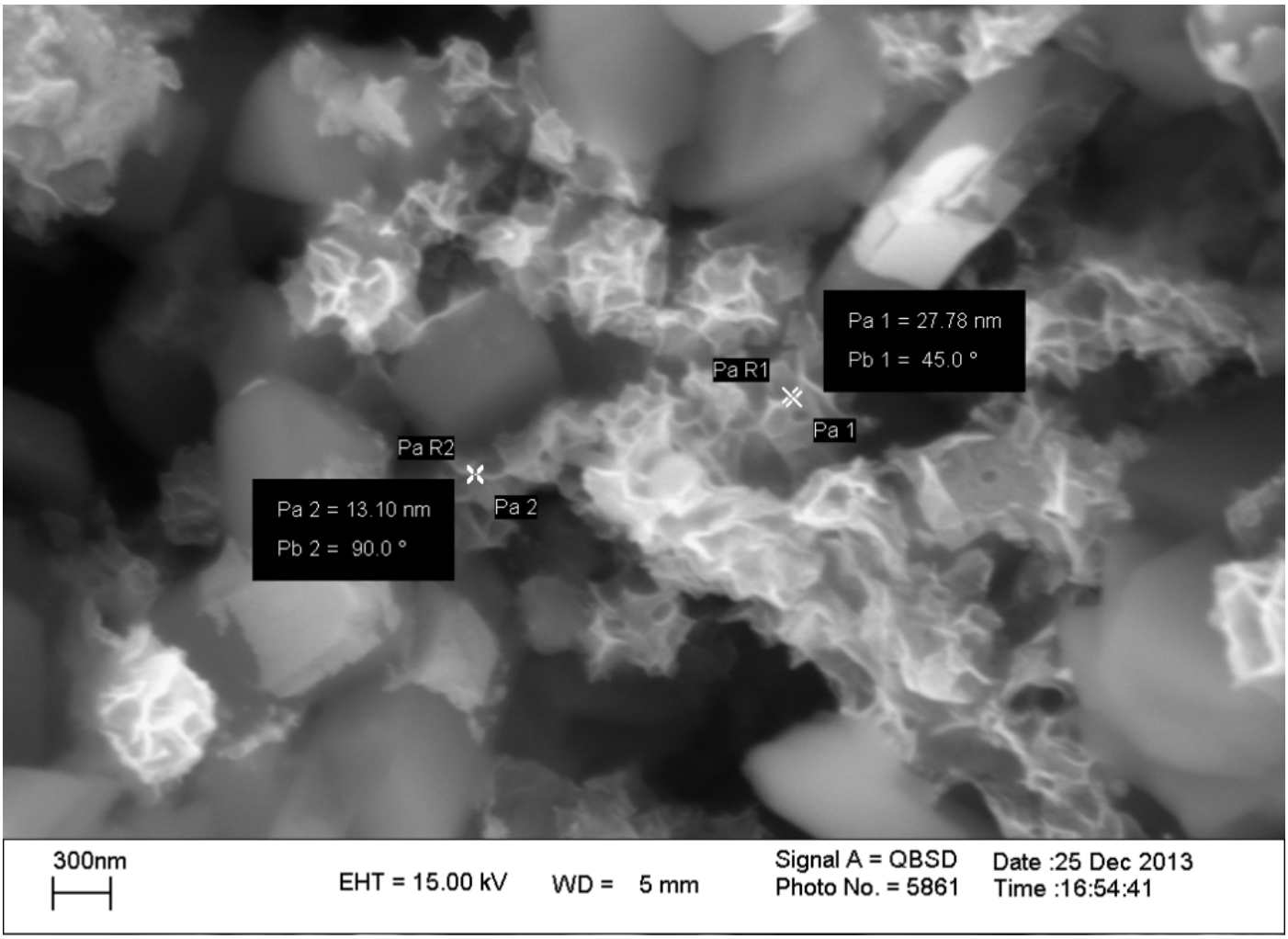
a


2µm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 5862
Date :25 Dec 2013
Time :16:56:43

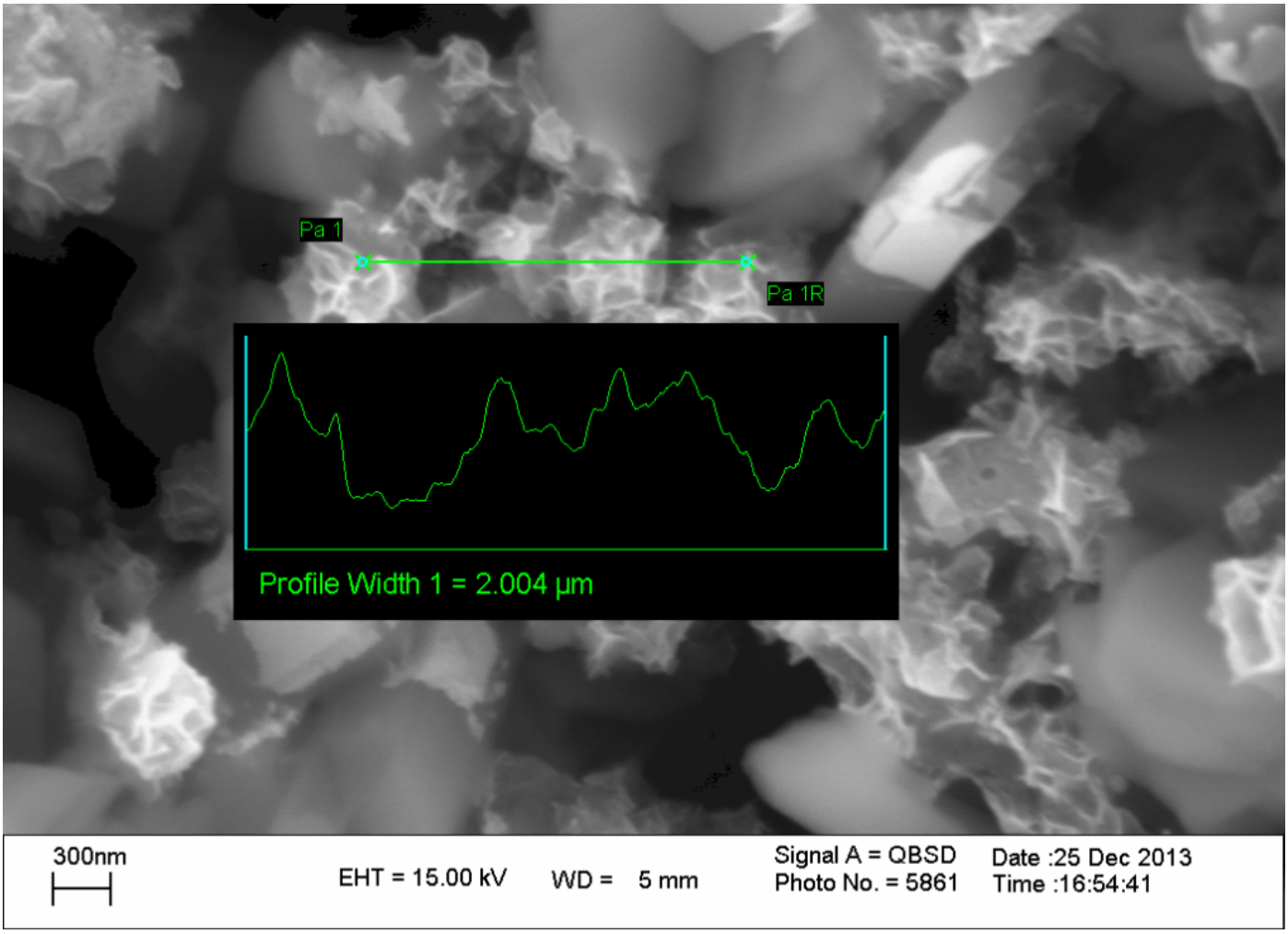
b


2µm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 5863
Date :25 Dec 2013
Time :16:58:19

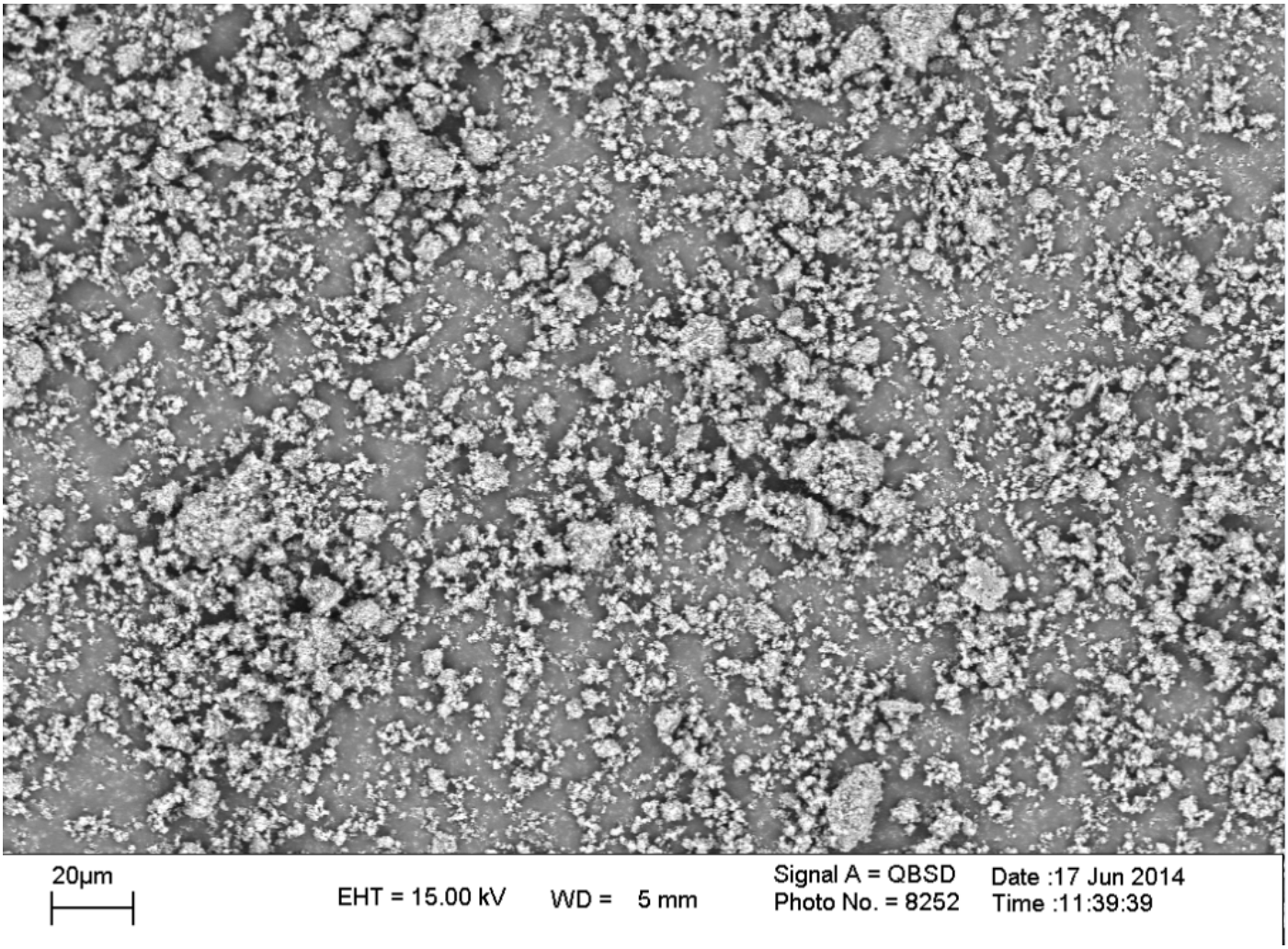
c


Pa 1 = 27.78 nm
Pb 1 = 45.0 °
Pa R1
Pa 1
Pa R2
Pa 2 = 13.10 nm
Pb 2 = 90.0 °
Pa 2
300nm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 5861
Date :25 Dec 2013
Time :16:54:41

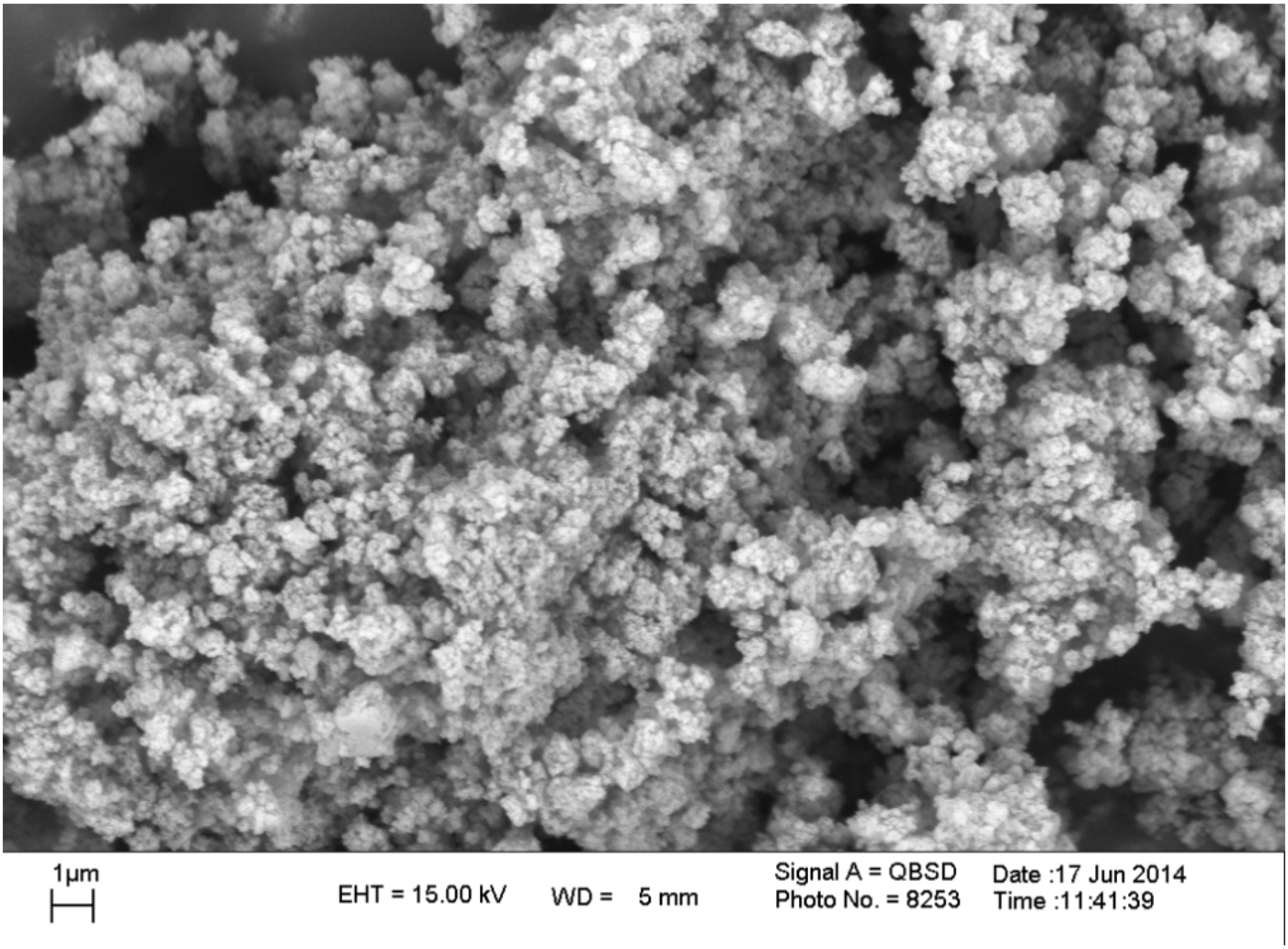
d


Pa 1
Pa 1R
Profile Width 1 = 2.004 µm
300nm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 5861
Date :25 Dec 2013
Time :16:54:41

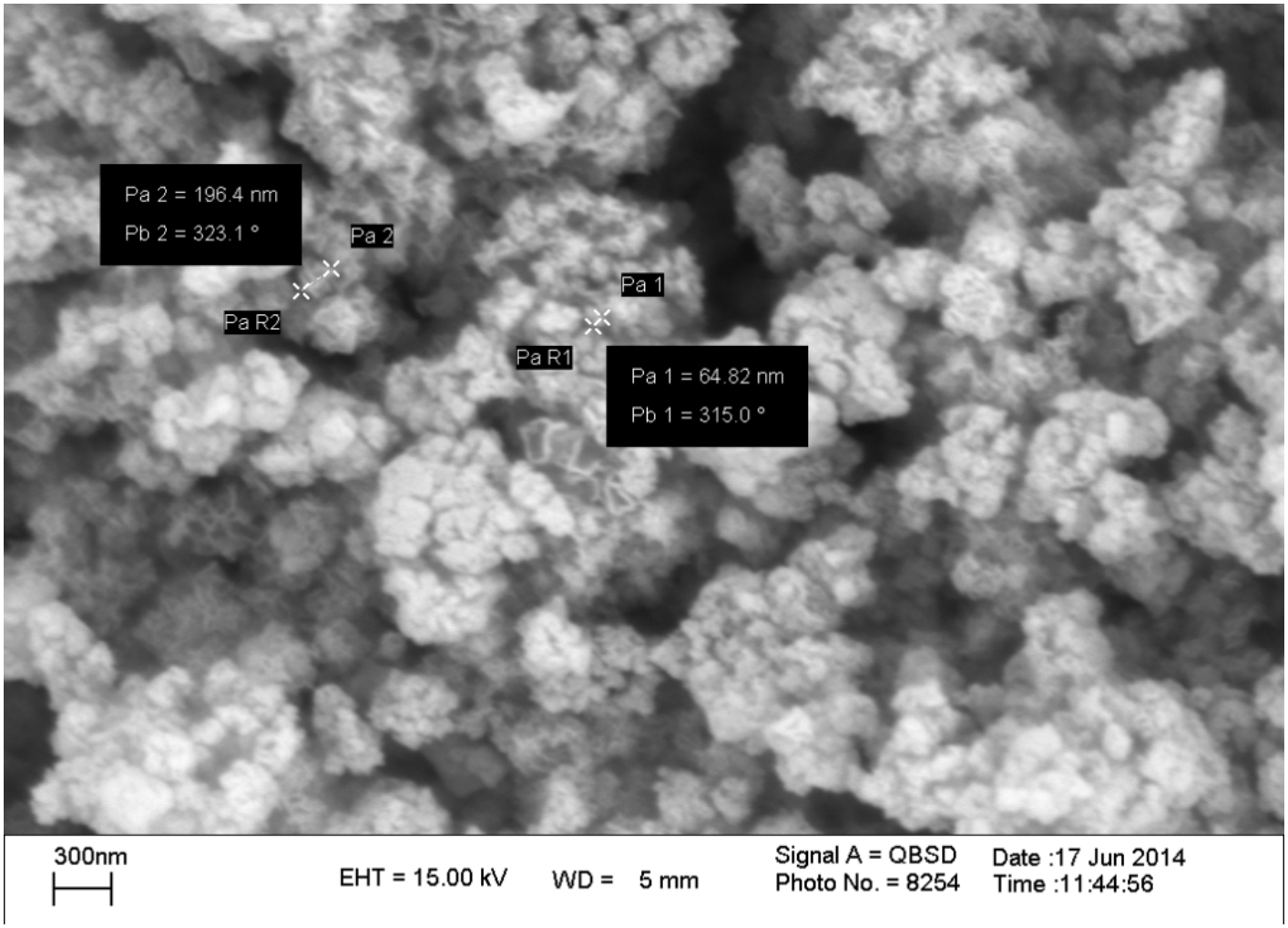
e


20µm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 8252
Date :17 Jun 2014
Time :11:39:39

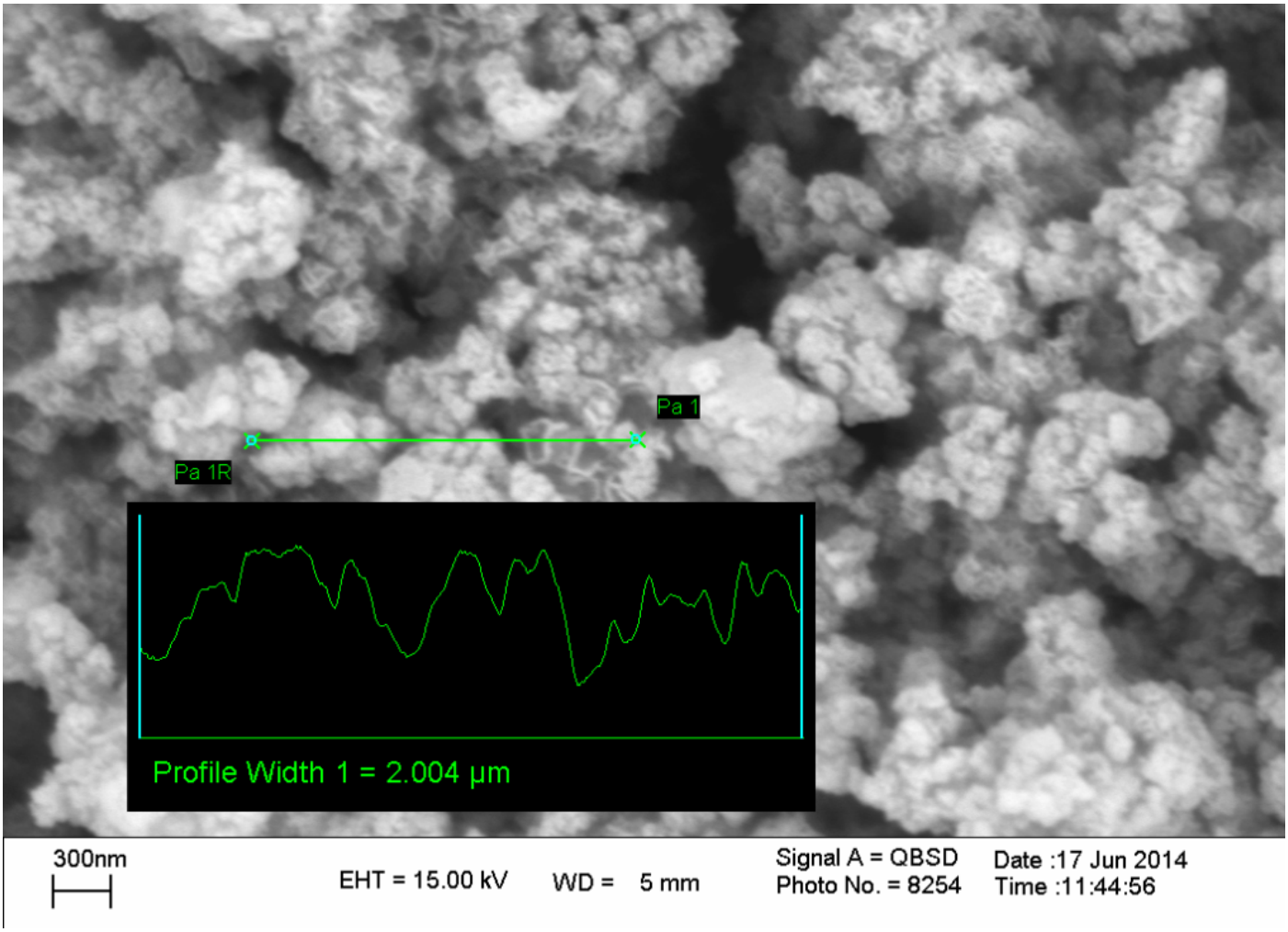
f


1µm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 8253
Date :17 Jun 2014
Time :11:41:39

g


Pa 2 = 196.4 nm
Pb 2 = 323.1 °
Pa 2
Pa R2
Pa 1
Pa R1
Pa 1 = 64.82 nm
Pb 1 = 315.0 °
300nm
EHT = 15.00 kV
WD = 5 mm
Signal A = QBSD
Photo No. = 8254
Date :17 Jun 2014
Time :11:44:56

h



i

Fig. S4 SEM images **6** (a-e) and **11** (f-i).