Supporting Information

Synthesis of Birnessite in the Presence of Phosphate, Silicate or Sulfate

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Sample	Before washed by 1 M KOH		After washed by 1 M KOH	
	Chemical Composition	SSA (m^2 g^{-1})	Chemical Composition	SSA (m^2 g^{-1})
Control	$K_{0.20}MnO_{2.05}\cdot 0.61H_2O$	30.1	-	-
P0.02	$K_{0.22}MnO_{2.03}(PO_4)_{0.016}\cdot 0.66H_2O$	34.0	$K_{0.26}MnO_{2.07}(PO_4)_{0.001}\cdot 0.66H_2O$	-
P0.05	$K_{0.24}MnO_{1.95}(PO_4)_{0.042}\cdot 0.71H_2O$	33.9	$K_{0.29}MnO_{2.06}(PO_4)_{0.002}\cdot 0.67H_2O$	-
P0.10	$K_{0.22}MnO_{1.81}(PO_4)_{0.098}\cdot 0.84H_2O$	27.9	$K_{0.31}MnO_{2.05}(PO_4)_{0.002}\cdot 0.72H_2O$	-
P0.20	$K_{0.19}MnO_{1.68}(PO_4)_{0.162}\cdot 0.93H_2O$	27.6	-	-
P0.30	$K_{0.26}MnO_{1.49}(PO_4)_{0.296}\cdot 1.13H_2O$	26.8	$K_{0.29}MnO_{2.03}(PO_4)_{0.001}\cdot 0.69H_2O$	22.8
Si0.20	$Na_{0.028}K_{0.16}MnO_{1.85}(SiO_4)_{0.061}\cdot 0.55H_2O$*	59.2	$Na_{0.010}K_{0.21}MnO_{2.01}(SiO_4)_{0.002}\cdot 0.58H_2O$	-
Si1.00	$Na_{0.071}K_{0.15}MnO_{1.76}(SiO_4)_{0.107}\cdot 0.78H_2O$	76.1	$Na_{0.003}K_{0.24}MnO_{1.99}(SiO_4)_{0.004}\cdot 0.62H_2O$	63.7
S0.20	$K_{0.21}MnO_{2.01}$ $(SO_4)_{0.005}\cdot 0.60H_2O$	33.2	$K_{0.23}MnO_{2.04}(SO_4)_{0.003}\cdot 0.56H_2O$	-
S1.00	$K_{0.16}MnO_{1.95}(SO_4)_{0.013}\cdot 0.65H_2O$	34.0	$K_{0.23}MnO_{2.05}(SO_4)_{0.004}\cdot 0.58H_2O$	32.5

Table S1. Chemical Composition and Specific Surface Area (SSA) of Birnessite Products

*The silicate series contain Na because of the use of sodium silicate in the synthesis.

Table S2. Estimation of Thicknesses of Birnessite Crystals in the Stacking Direction and the Number of the Stacking Sheets Based on (001) Diffraction Peaks Using the Scherer Equation

Sample	Before washed by 1 M KOH		After washed by 1 M KOH	
	Thickness (nm)	Number of Stacked Sheets	Thickness (nm)	Number of Stacked Sheets
Control	6.42	10	-	-
P0.02	3.57	6	4.19	7
P0.05	1.44	3	2.89	5
P0.10	< 1.44	1 or 2	0.77	2
P0.30	< 1.44	1 or 2	1.31	3
Si0.02	5.40	8	5.42	8
Si0.20	4.31	7	5.39	8
Si1.00	2.70	5	3.48	6
S1.00	5.39	8	5.40	8

Table S3. The D-Spacing Ratio of (11, 20) Peak to (31, 02) Peak of Birnessite Products

Sample	Unwashed	Washed	Sample	Unwashed	Washed	Sample	Unwashed	Washed
	d-spacing ratio			d-spacing ratio			d-spacing ratio	
Control	1.728	-						
P0.02	1.726	1.724	Si0.02	1.725	1.725	S0.02	1.728	-
P0.05	1.723	1.721	Si0.05	1.725	-	S0.05	1.728	-
P0.10	1.716	1.715	Si0.10	1.725	-	S0.10	1.728	-
P0.20	1.713	-	Si0.20	1.725	1.725	S0.20	1.728	-
P0.30	1.719	1.714	Si1.00	1.717	1.717	S0.50	1.727	-
						S1.00	1.726	1.724

Table S4. Results of the Mn K-edge XANES Linear Combination Fitting

Sample	Mn references						Statistics	
	$MnSO_4$	Feitknechtite	Manganite	Mn_2O_3	KBi[a]	δ-MnO_2	χ^2	Red χ^2
Control	0.03[b]	0.03	0.00	0.00	0.32	0.59	0.05	3.40E-05
P0.02	0.02	0.07	0.00	0.00	0.32	0.57	0.02	1.15E-05
P0.02*	0.00	0.06	0.00	0.00	0.41	0.46	0.03	1.84E-05
P0.05	0.01	0.18	0.00	0.00	0.25	0.54	0.02	1.10E-05
P0.05*	0.00	0.17	0.00	0.00	0.26	0.55	0.04	2.73E-05
P0.10	0.02	0.25	0.00	0.00	0.08	0.60	0.03	1.98E-05
P0.10*	0.00	0.21	0.00	0.00	0.21	0.57	0.04	3.09E-05
P0.20	0.02	0.25	0.00	0.06	0.01	0.65	0.08	5.38E-05
P0.30	0.00	0.24	0.00	0.16	0.00	0.61	0.34	2.42E-04
P0.30*	0.00	0.16	0.06	0.00	0.21	0.55	0.05	3.71E-05
Si0.20	0.03	0.03	0.16	0.00	0.25	0.50	0.05	3.86E-05
Si0.20*	0.00	0.18	0.00	0.00	0.27	0.51	0.08	5.64E-05
Si1.00	0.00	0.26	0.00	0.00	0.36	0.35	0.05	3.49E-05
Si1.00*	0.00	0.01	0.23	0.01	0.00	0.74	0.13	9.67E-05
S0.20	0.02	0.00	0.14	0.00	0.30	0.50	0.04	2.79E-05
S0.20*	0.00	0.01	0.13	0.00	0.31	0.48	0.06	4.34E-05
S1.00	0.04	0.00	0.15	0.00	0.31	0.47	0.08	5.58E-05
S1.00*	0.00	0.02	0.10	0.00	0.39	0.46	0.03	2.42E-05

*The samples are washed by 1 M KOH. [a]KBi represents potassium birnessite.

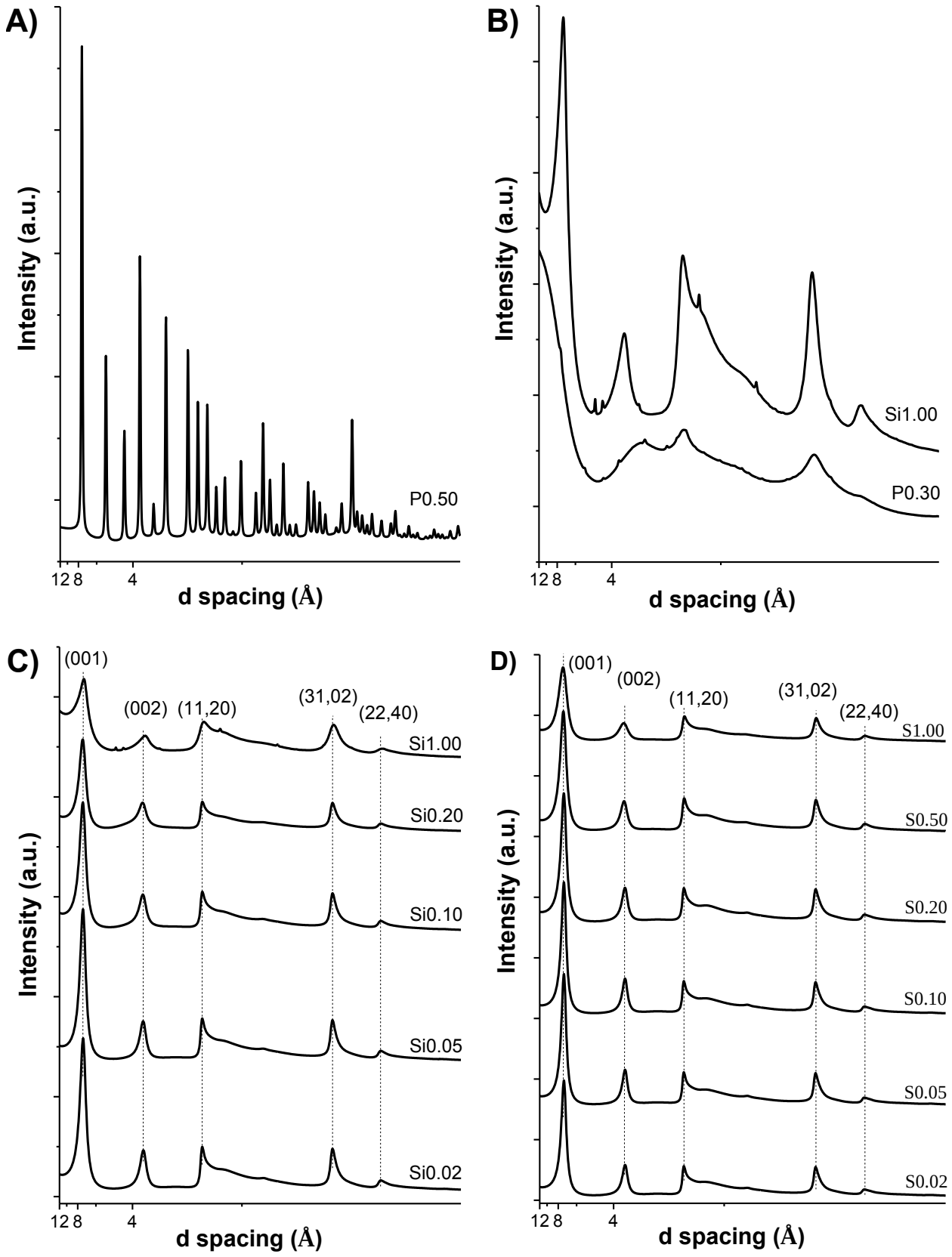
Table S5. Manganese K-edge EXAFS Shell-by-Shell Fitting Parameters of Birnessite Products

Samples	Unwashed by 1 M KOH						Washed by 1 M KOH				
	Shell	CN	r (Å)	σ^2 (Å^2)	ΔE (eV)	R	CN	r (Å)	σ^2 (Å^2)	ΔE (eV)	R
Control	Mn-O	6.9(0.5)*	1.92 (0.00)	0.006 (0.001)	3.2 (0.7)	0.0017					
	Mn-Mn	6.5 (0.6)	2.88 (0.00)	0.007 (0.001)							
	Mn-Mn	1.0 (0.5)	3.49 (0.03)	0.007 (0.001)							
P0.02	Mn-O	6.8 (0.5)	1.92 (0.00)	0.006 (0.001)	3.2 (0.7)	0.0018	6.8 (0.5)	1.92 (0.00)	0.006 (0.001)	3.3 (0.7)	0.0018
	Mn-Mn	6.4 (0.6)	2.88 (0.00)	0.007 (0.001)			6.4 (0.6)	2.88 (0.00)	0.007 (0.001)		
	Mn-Mn	0.9 (0.5)	3.48 (0.03)	0.007 (0.001)			0.9 (0.5)	3.47 (0.03)	0.007 (0.001)		
P0.05	Mn-O	6.7 (0.5)	1.91 (0.00)	0.006 (0.001)	2.7 (0.7)	0.0015	6.9 (0.4)	1.91 (0.00)	0.006 (0.000)	2.9 (0.6)	0.0012
	Mn-Mn	5.7 (0.6)	2.88 (0.00)	0.007 (0.001)			6.2 (0.5)	2.88 (0.00)	0.007 (0.001)		
	Mn-Mn	0.9 (0.4)	3.45 (0.03)	0.007 (0.001)			0.8 (0.4)	3.43 (0.03)	0.007 (0.001)		
P0.10	Mn-O	6.6 (0.4)	1.91 (0.00)	0.006 (0.000)	2.3 (0.6)	0.0014	7.2 (0.6)	1.91 (0.00)	0.007 (0.001)	2.2 (0.8)	0.0023
	Mn-Mn	5.6 (0.6)	2.87 (0.00)	0.008 (0.001)			5.5 (0.6)	2.87 (0.00)	0.007 (0.001)		
	Mn-Mn	1.3 (0.4)	3.44 (0.02)	0.008 (0.001)			1.0 (0.4)	3.43 (0.03)	0.007 (0.001)		
P0.20	Mn-O	6.2 (0.4)	1.91 (0.00)	0.006 (0.001)	2.3 (0.7)	0.0017					
	Mn-Mn	5.5 (0.6)	2.87 (0.00)	0.006 (0.001)							
	Mn-Mn	0.9 (0.5)	3.46 (0.03)	0.006 (0.001)							
P0.30	Mn-O	6.0 (0.3)	1.91 (0.00)	0.005 (0.000)	2.2 (0.7)	0.0014	6.6 (0.6)	1.92 (0.00)	0.006 (0.001)	2.8 (0.8)	0.0025
	Mn-Mn	5.3 (0.6)	2.87 (0.03)	0.011 (0.003)			5.6 (0.7)	2.88 (0.01)	0.007 (0.001)		
	Mn-Mn	0.4 (0.3)	3.02 (0.03)	0.011 (0.003)			0.8 (0.5)	3.42 (0.04)	0.007 (0.001)		
Si0.20	Mn-O	6.4 (0.7)	1.92 (0.01)	0.006 (0.001)	3.7 (1.0)	0.0042	6.8 (0.6)	1.92 (0.00)	0.006 (0.001)	3.0 (0.8)	0.0021
	Mn-Mn	6.3 (0.9)	2.89 (0.01)	0.007 (0.001)			6.9 (0.7)	2.88 (0.00)	0.007 (0.001)		
	Mn-Mn	1.2 (0.8)	3.49 (0.04)	0.007 (0.001)			0.8 (0.6)	3.47 (0.04)	0.007 (0.001)		
Si1.00	Mn-O	6.5 (0.7)	1.92 (0.01)	0.005 (0.001)	2.9 (1.2)	0.0103	7.1 (0.6)	1.91 (0.01)	0.006 (0.001)	3.8 (1.3)	0.0070
	Mn-Mn	5.6(0.6)	2.88 (0.01)	0.009 (0.002)			6.4 (0.7)	2.88 (0.01)	0.007 (0.001)		
	Mn-Mn	0.9(0.5)	3.51 (0.06)	0.009 (0.002)			1.0 (0.6)	3.48 (0.06)	0.007 (0.001)		

Table S5. Manganese K-edge EXAFS Shell-by-Shell Fitting Parameters of Birnessite Products (*Continued*)

Samples	Unwashed by 1 M KOH						Washed by 1 M KOH				
	Shell	CN	r (Å)	σ^2 (Å^2)	ΔE (eV)	R	CN	r (Å)	σ^2 (Å^2)	ΔE (eV)	R
S0.20	Mn-O	6.8 (0.6)	1.92 (0.00)	0.006 (0.001)	3.3 (0.7)	0.0020	6.8 (0.5)	1.92 (0.00)	0.006 (0.001)	3.3 (0.6)	0.0015
	Mn-Mn	6.3 (0.6)	2.88(0.00)	0.007 (0.001)			7.0 (0.6)	2.88 (0.00)	0.008 (0.001)		
	Mn-Mn	1.3 (0.5)	3.48 (0.02)	0.007 (0.001)			1.0 (0.5)	3.49 (0.03)	0.008 (0.001)		
S1.00	Mn-O	6.7 (0.6)	1.92 (0.00)	0.006 (0.001)	3.1 (0.9)	0.0028	6.8 (0.5)	1.92 (0.00)	0.006 (0.001)	3.5 (0.7)	0.0018
	Mn-Mn	6.0 (0.7)	2.97 (0.01)	0.007 (0.001)			6.4 (0.6)	2.88 (0.00)	0.007 (0.001)		
	Mn-Mn	1.1 (0.6)	3.48 (0.03)	0.007 (0.001)			0.7 (0.5)	3.460.04)	0.007 (0.001)		

* Errors are given in parentheses. Coordination numbers (CN), interatomic distances (r), Debye-Waller factors (σ^2), and energy shift (ΔE) were obtained by fitting the EXAFS spectra to the standard EXAFS equation.


A)
Intensity (a.u.)
P0.50
12 8
4
d spacing (Å)
B)
Intensity (a.u.)
Si1.00
P0.30
12 8
4
d spacing (Å)
C)
(001)
(002)
(11,20)
(31,02)
(22,40)
Si1.00
Si0.20
Si0.10
Si0.05
Si0.02
Intensity (a.u.)
12 8
4
d spacing (Å)
D)
(001)
(002)
(11,20)
(31,02)
(22,40)
S1.00
S0.50
S0.20
S0.10
S0.05
S0.02
Intensity (a.u.)
12 8
4
d spacing (Å)

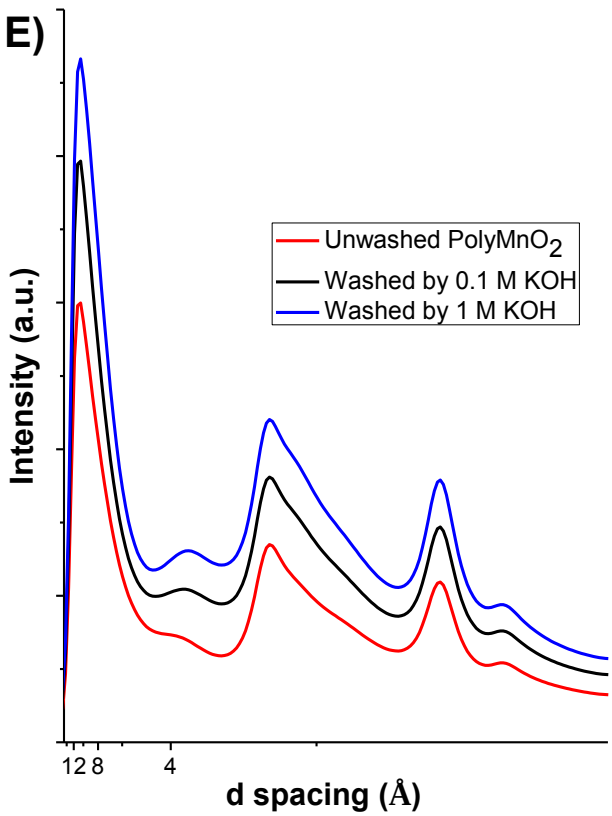
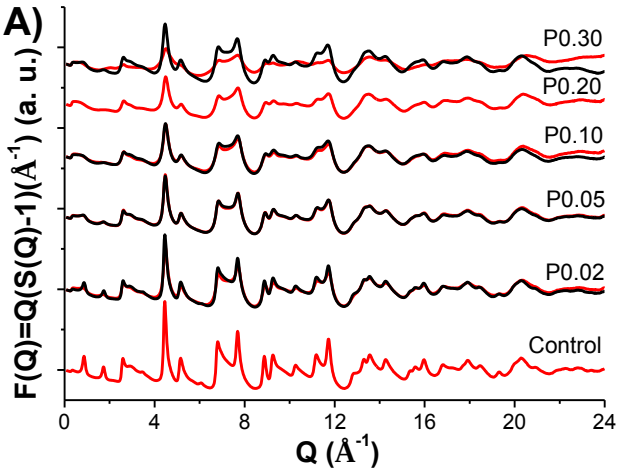
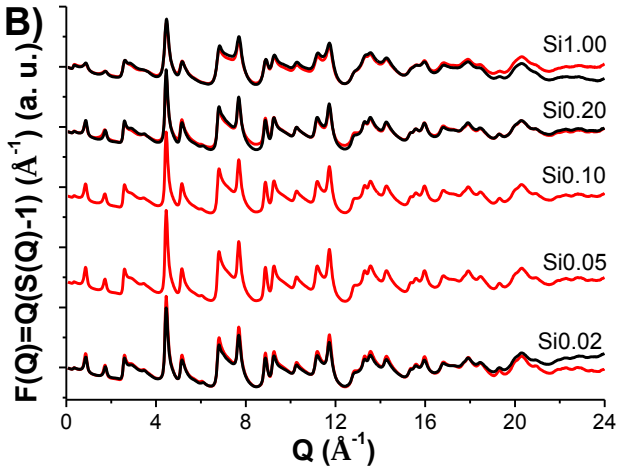


Figure S1. Powder XRD patterns of birnessite products. (A) P0.50. (B) P0.30 and Si1.00. (C) Si series. (D) S series. and (E) polyMnO$_2$.


A)
P0.30
P0.20
P0.10
P0.05
P0.02
Control
F(Q)=Q(S(Q)-1)(Å-1) (a. u.)
0
4
8
12
16
20
24
Q (Å-1)


B)
Si1.00
Si0.20
Si0.10
Si0.05
Si0.02
F(Q)=Q(S(Q)-1) (Å-1) (a. u.)
0
4
8
12
16
20
24
Q (Å-1)

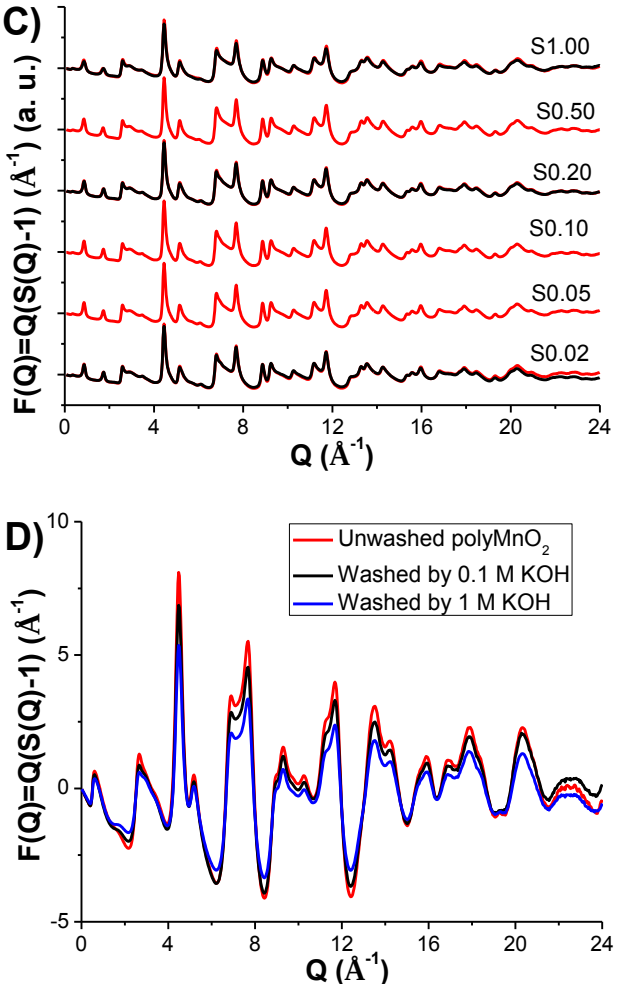


Figure S2. Reduced structure functions (F(Q)) of birnessite products. (A) P series. (B) Si series. (C) S series. D) polyMnO$_2$. Reduced structure functions of birnessite products (red) are superimposed with those of the corresponding KOH-washed products (black).

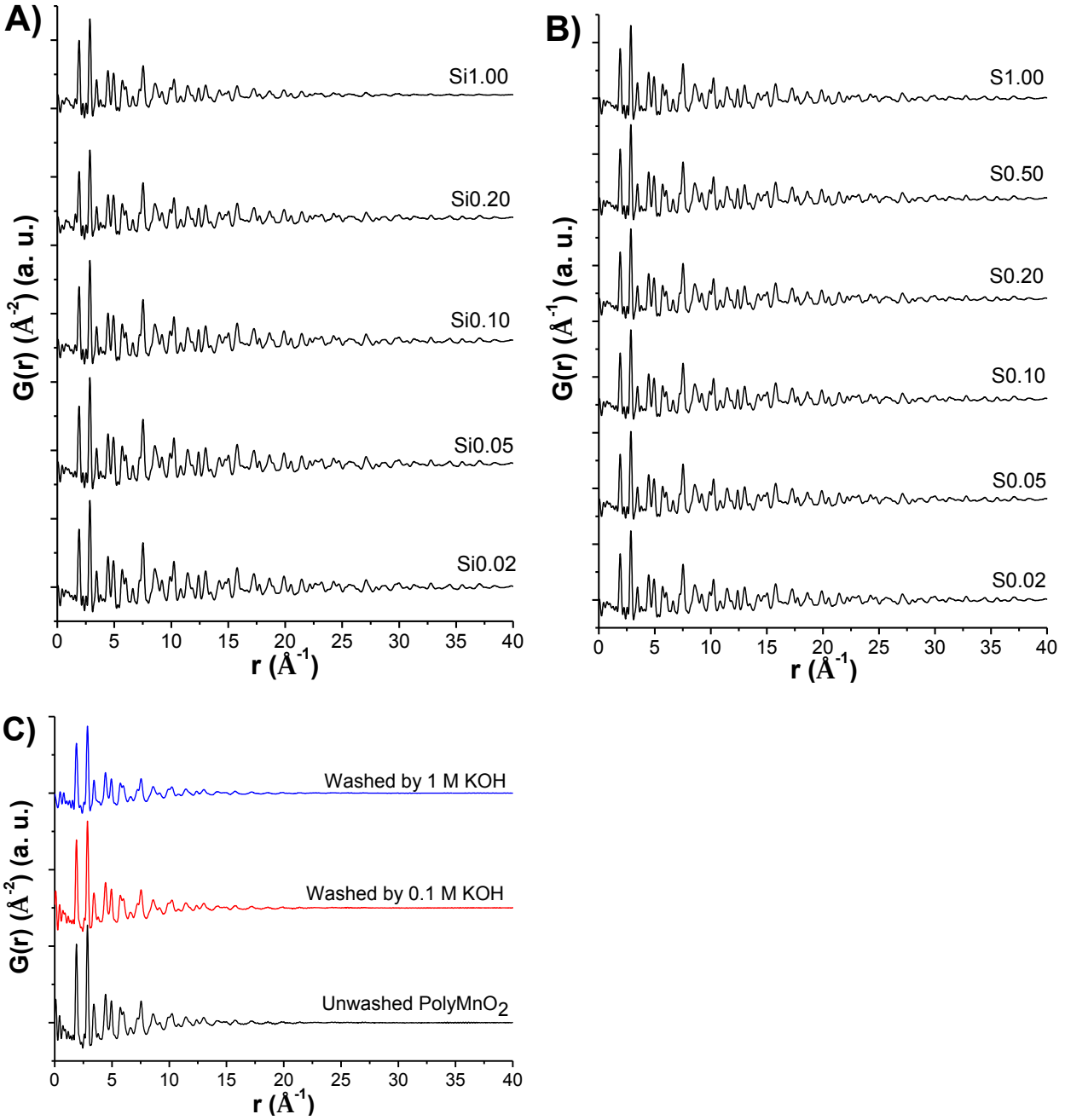
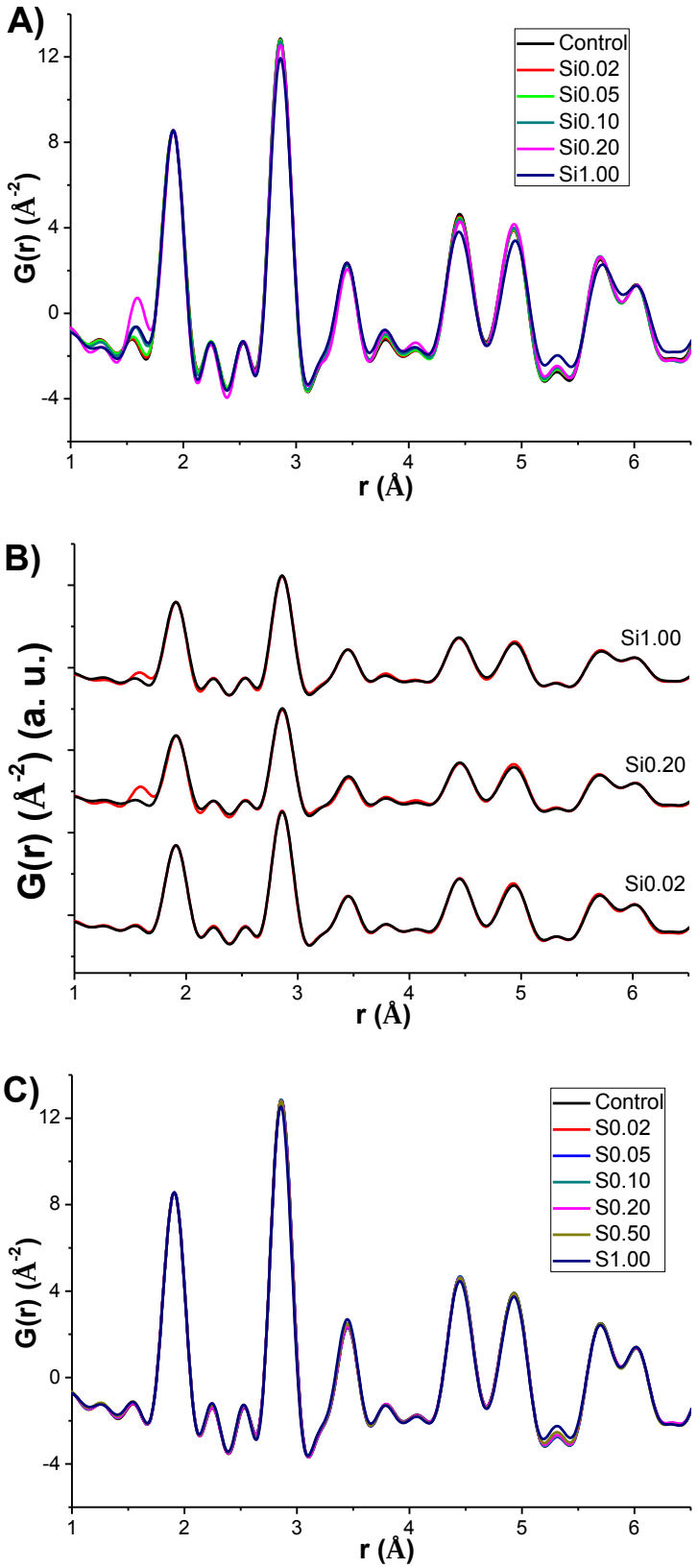


Figure S3. X-ray atomic pair distribution functions (*G(r)s*) of acid birnessite products and polyMnO$_2$. (A) Si series. (B) S series. (C) polyMnO$_2$.


A)
Control
Si0.02
Si0.05
Si0.10
Si0.20
Si1.00
G(r) (Å-2)
r (Å)
B)
Si1.00
Si0.20
Si0.02
G(r) (Å-2) (a. u.)
r (Å)
C)
Control
S0.02
S0.05
S0.10
S0.20
S0.50
S1.00
G(r) (Å-2)
r (Å)

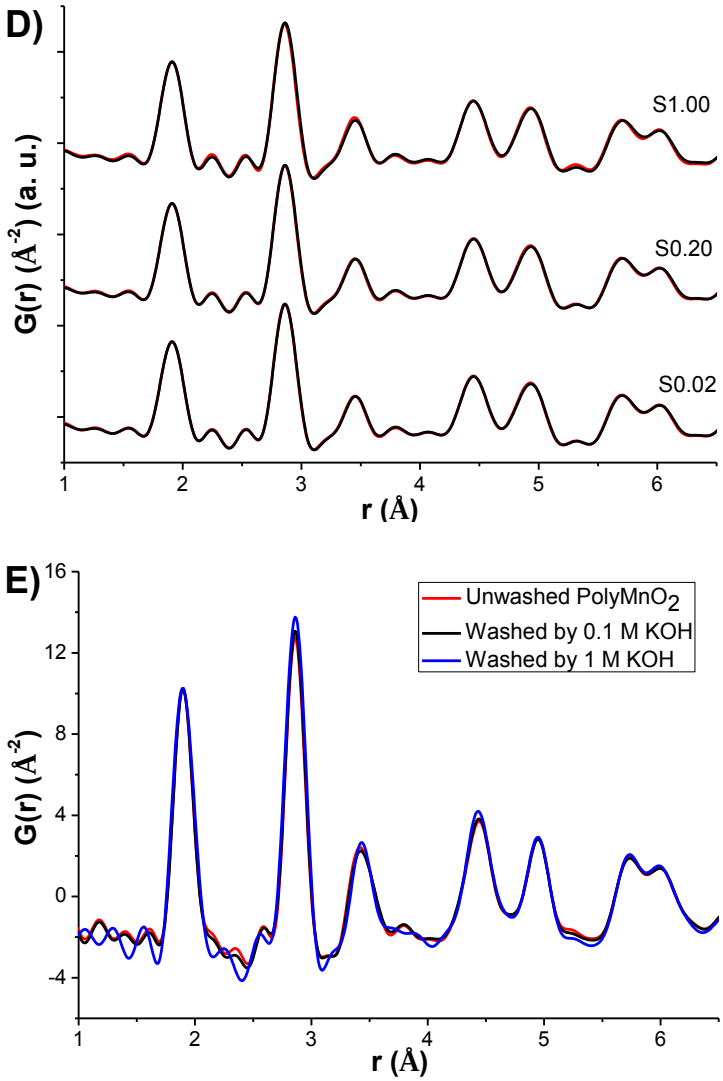


Figure S4. Pair distribution functions within 6.5 Å for birnessite products of the Si and S series and polyMnO$_2$ samples. The PDFs of birnessite products (red) are superimposed with those of the corresponding KOH-washed products (black).

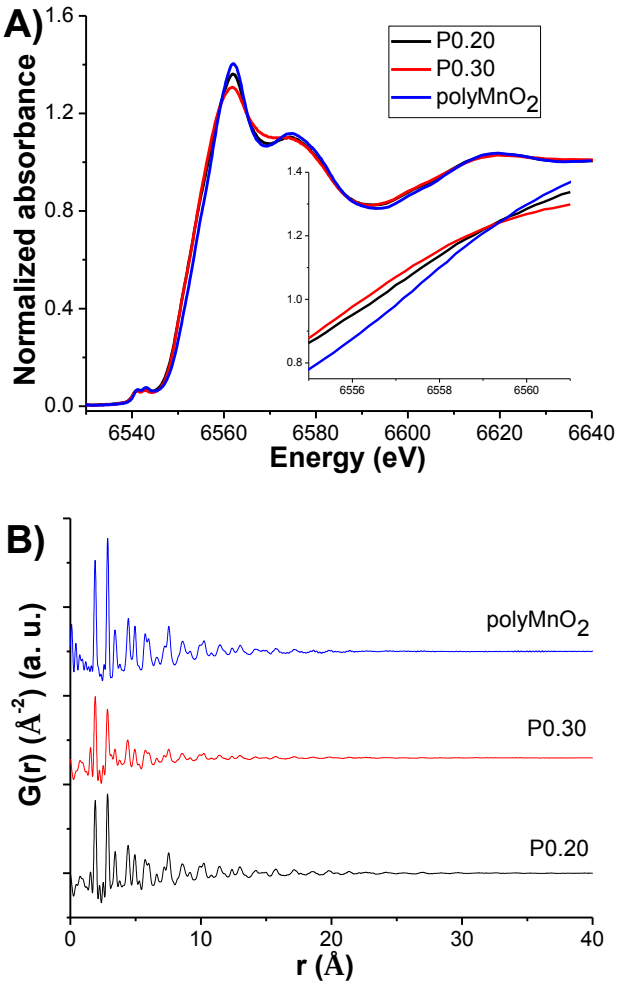


Figure S5. Mn K-edge XANES spectra (A) and pair distribution functions (B) for P0.20, P0.30 and polyMnO$_2$.

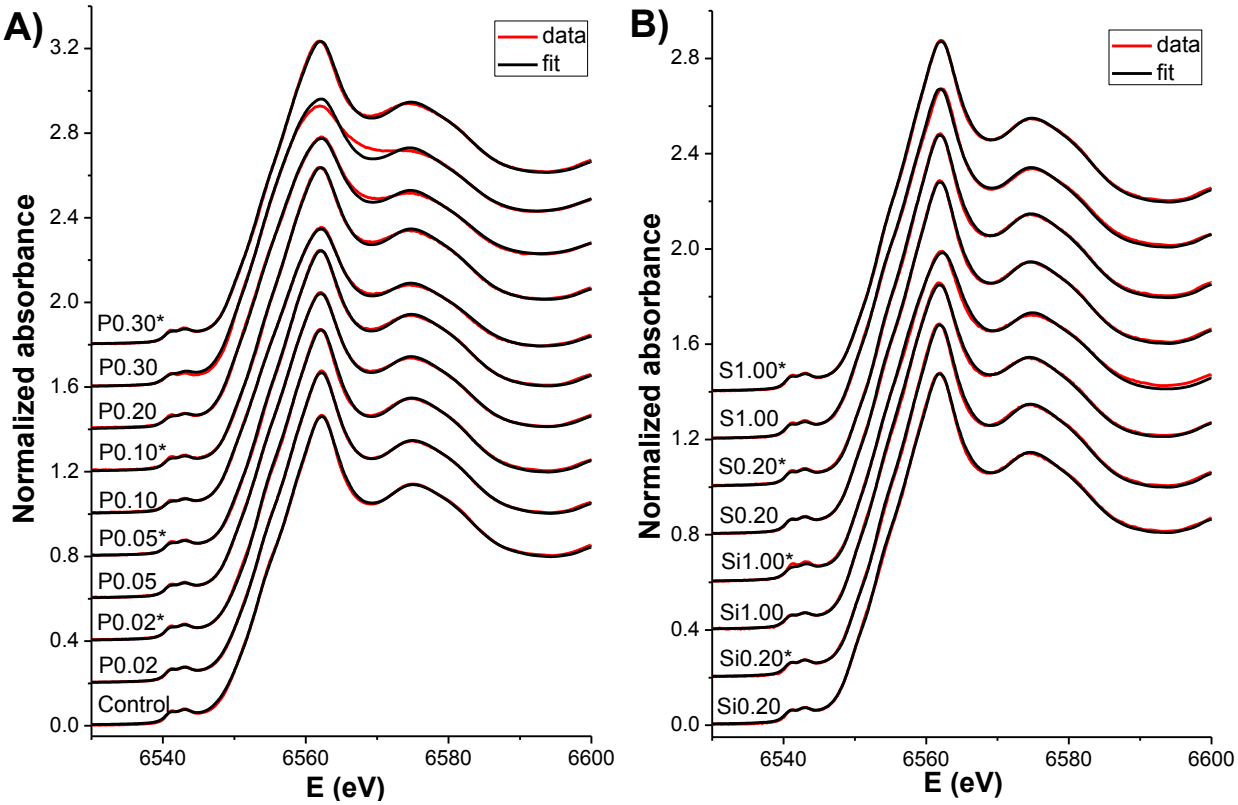
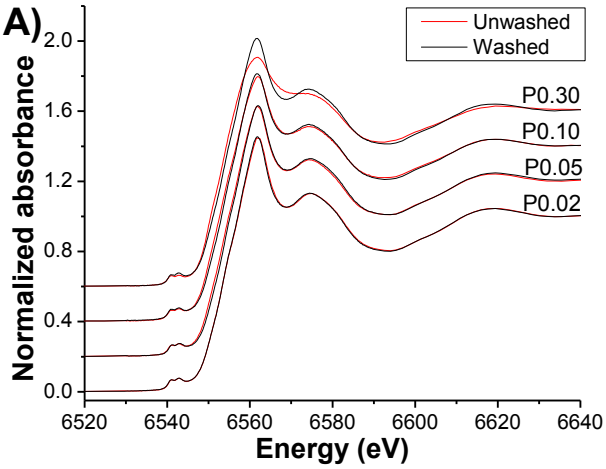


Figure S6. Comparison of Mn K-edge XANES spectra and their linear combination fits. (A) P series; (B) Si and S series. Asterisks denote the KOH-washed samples.



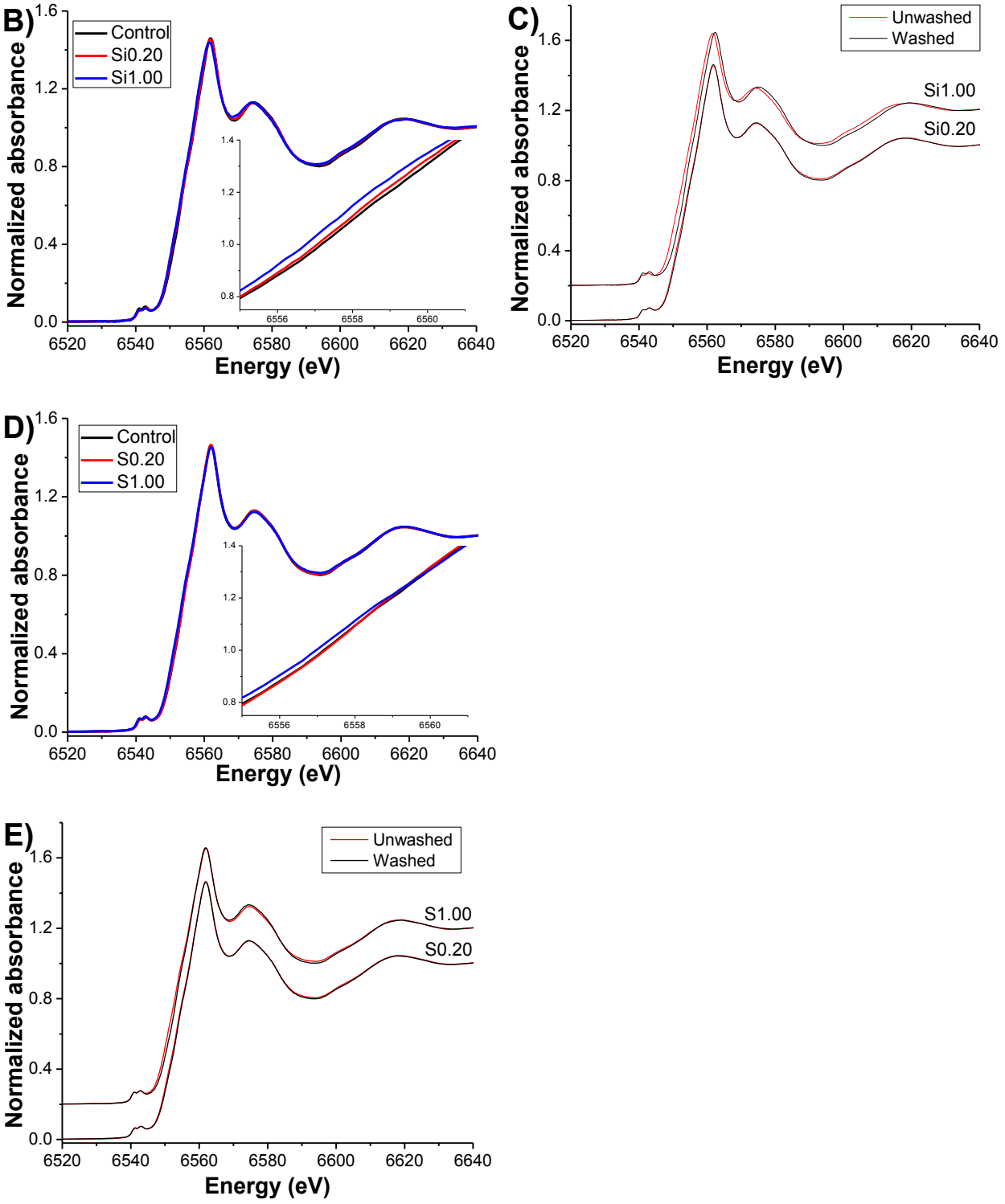


Figure S7. Mn K-edge XANES spectra of P (A), Si (B and C) and S (D and E) series samples. Spectra of birnessite products (black) are superimposed with those of the corresponding KOH-washed products (gray) (A, C, and E).

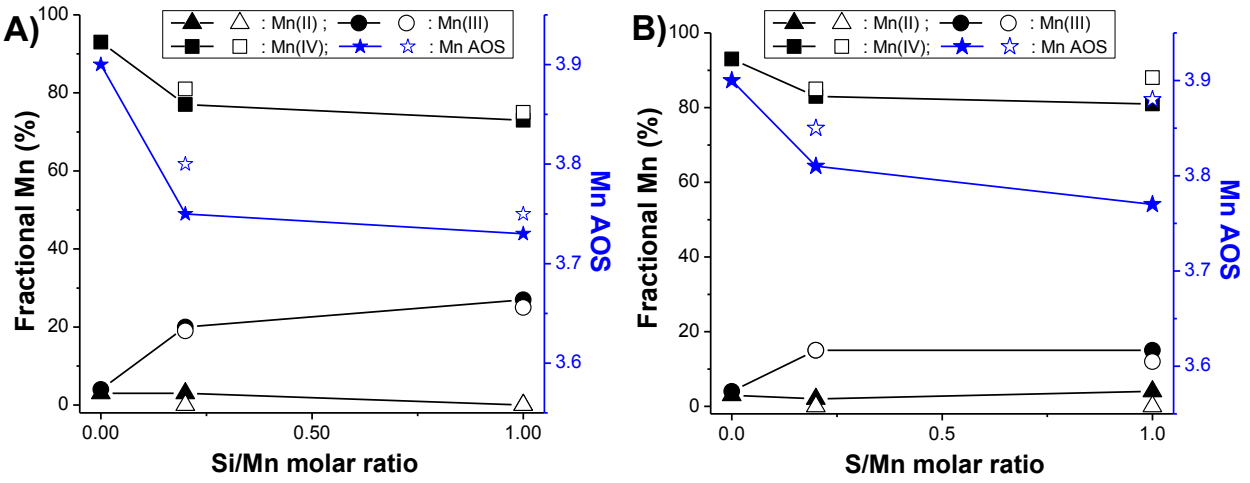


Figure S8. Percentage of each Mn valence state and Mn AOS of Si (A) and S (B) series samples. Filled symbols are for the products while the empty symbols for the corresponding KOH-washed products.

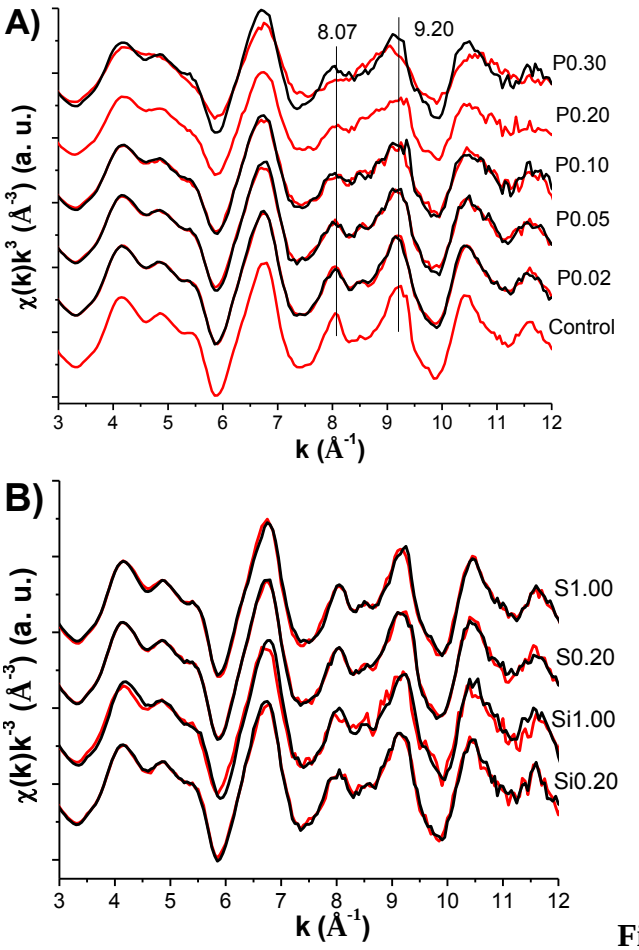


Figure S9. Mn K-edge k^3-weighted EXAFS of P (A), Si and S (B) series samples. Spectra of acid birnessite products (red) are superimposed with those of the corresponding KOH-washed products (black).

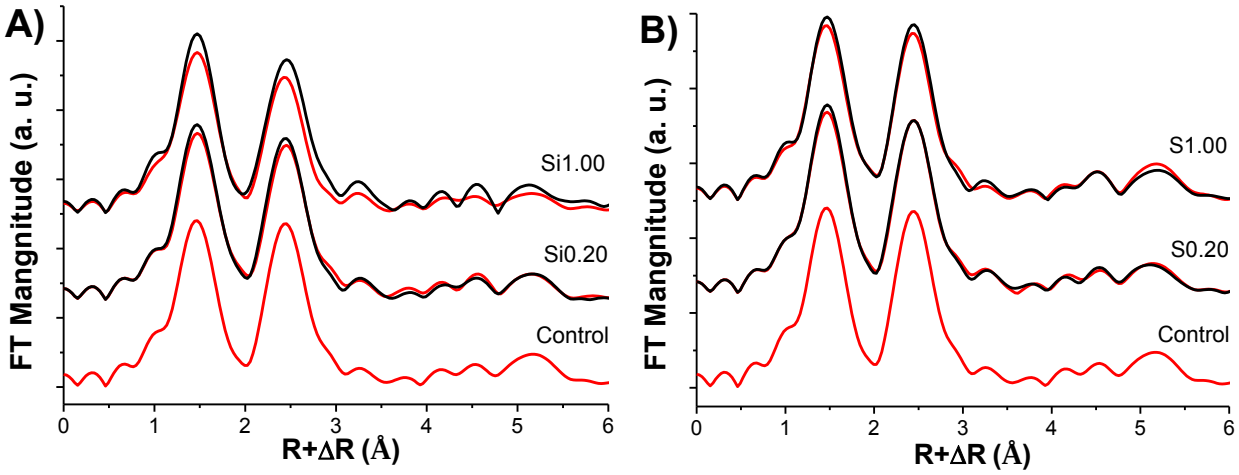
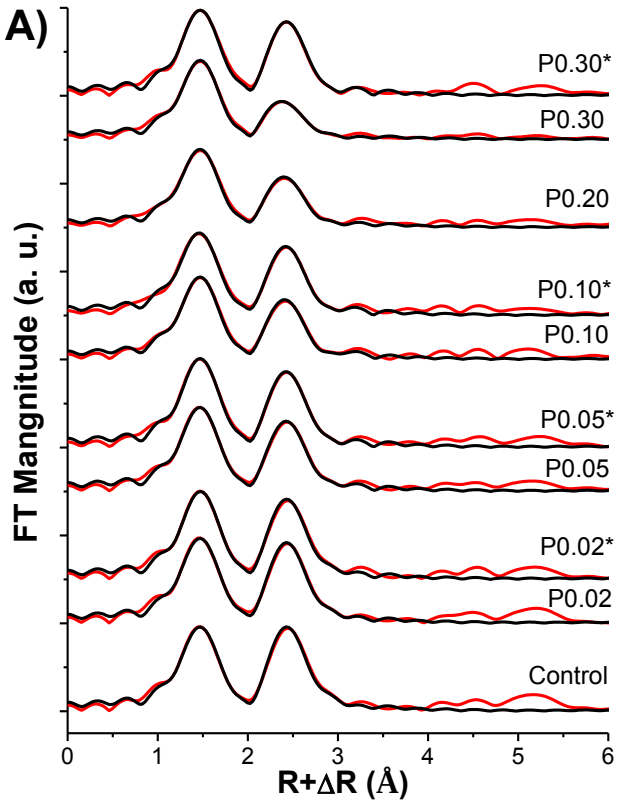


Figure S10. Magnitude of Fourier transformed Mn K-edge EXAFS spectra of the birnessites of the Si (A) and S (B) series. Spectra of birnessite products (red) are superimposed with those of the corresponding KOH-washed products (black).



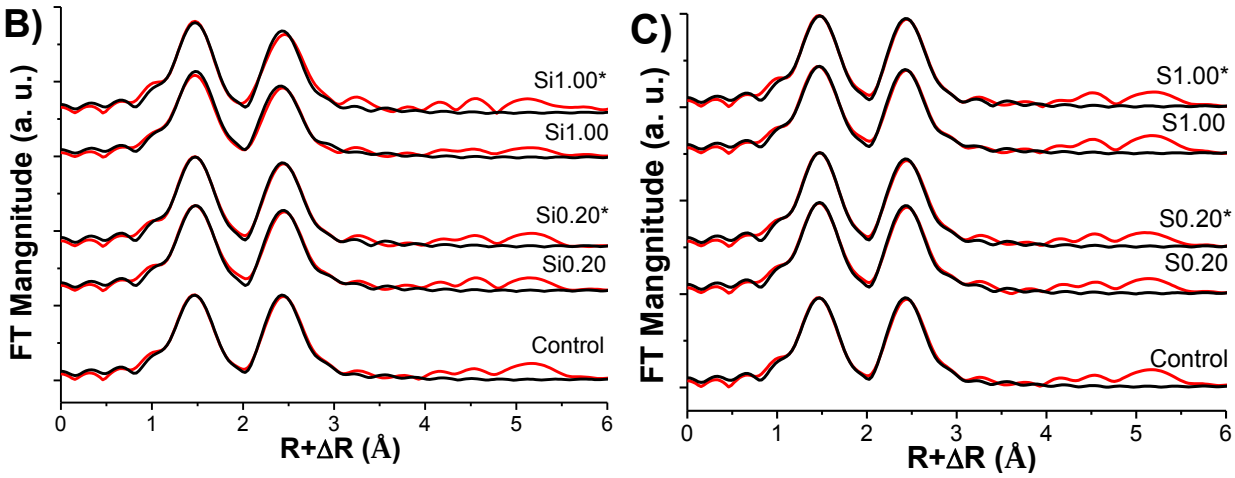
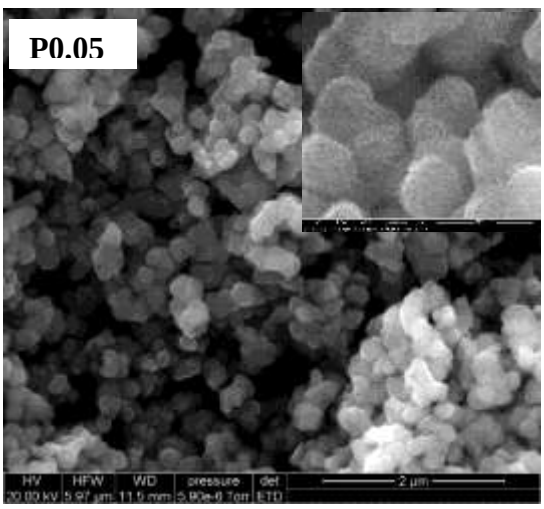
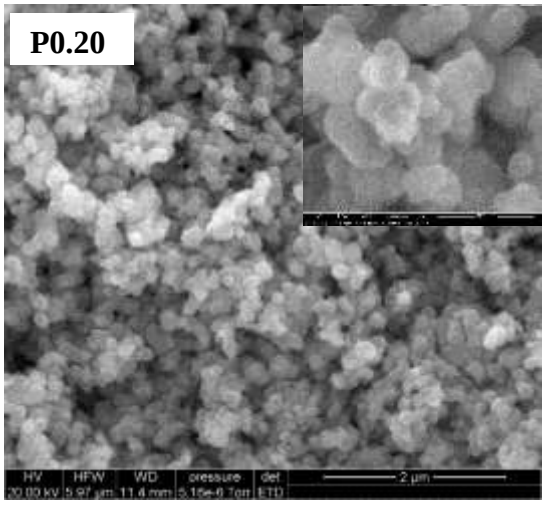
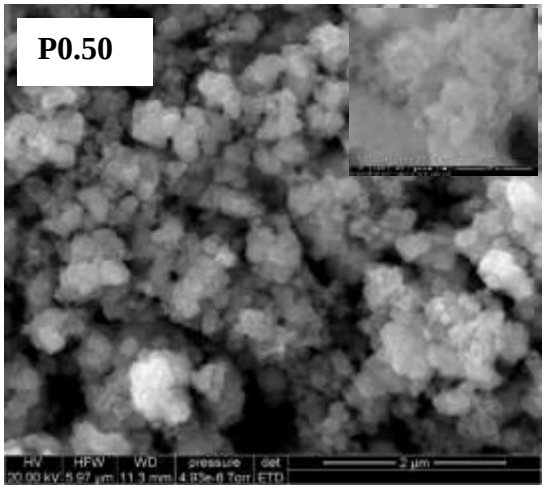


Figure S11. Comparison of shell-by-shell fits and the spectra of the birnessites of the P series (A), Si series (B) and S series (C). Spectra of birnessite products (red) are superimposed with the pattern of the corresponding fitting results (black). Asterisks denote that the samples were KOH washed.







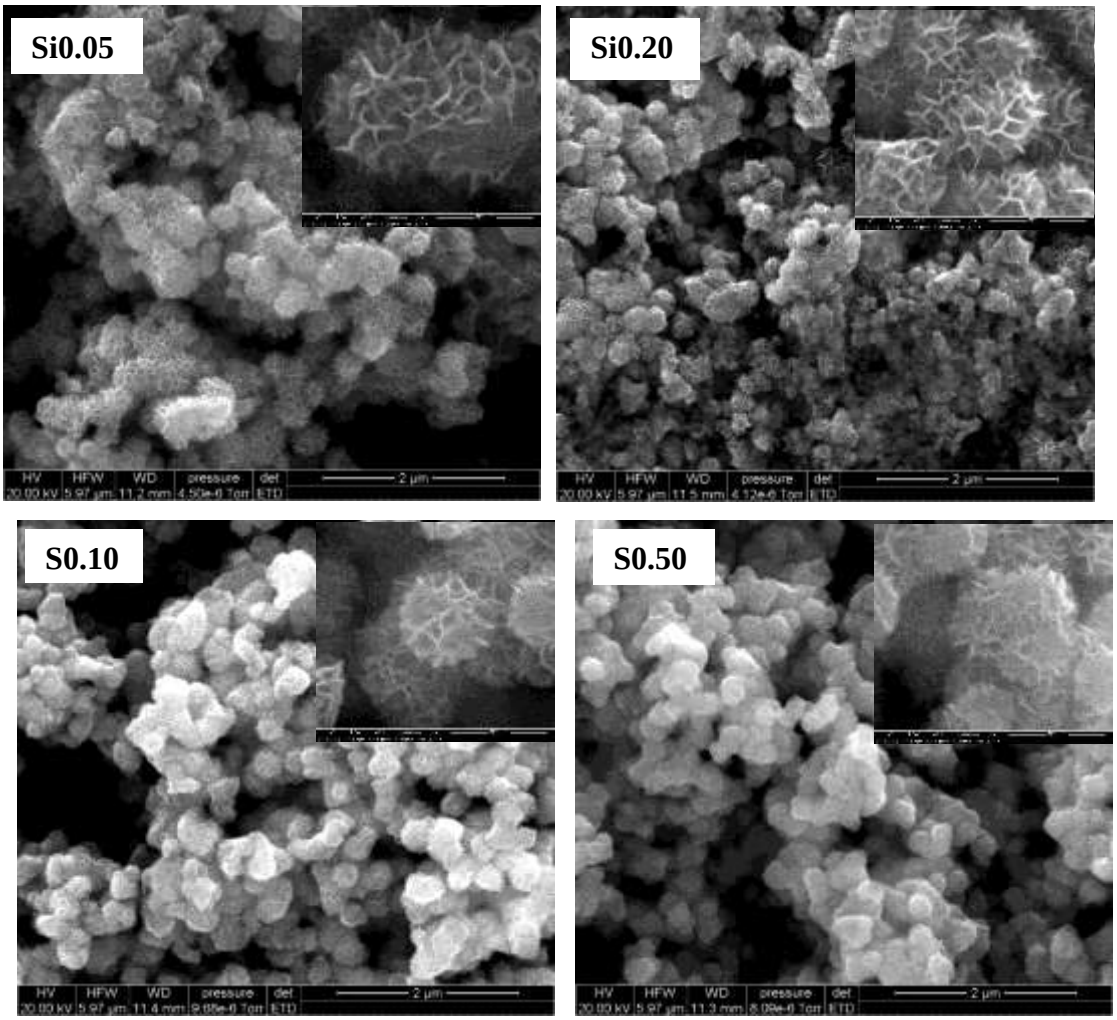
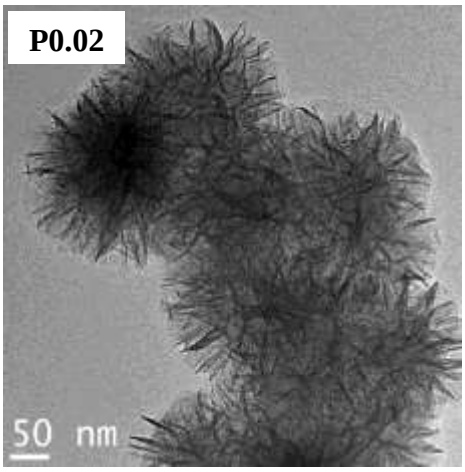
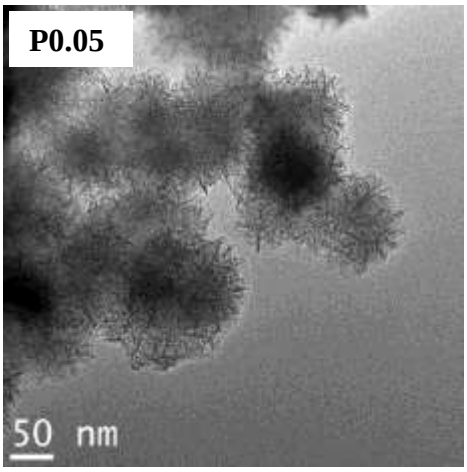
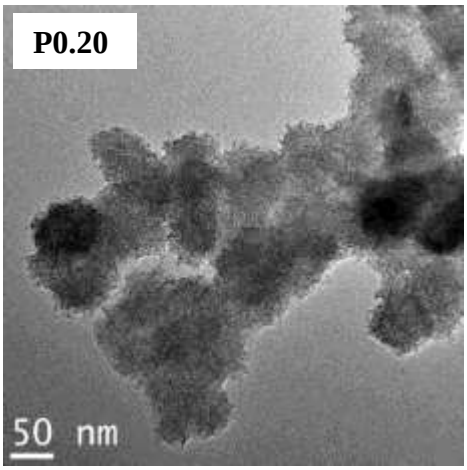
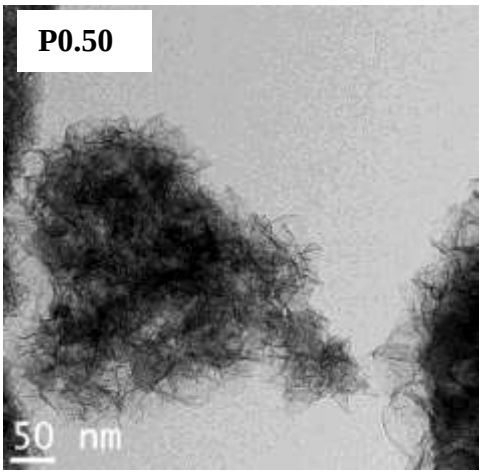


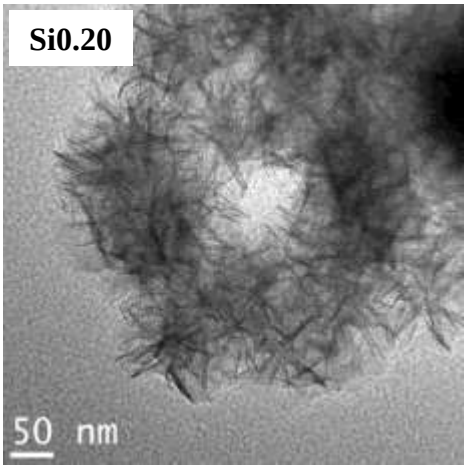
Figure S12. FE-SEM images of low and high magnification with scale bars of 2 µm and 300 nm (insets) for birnessite products.

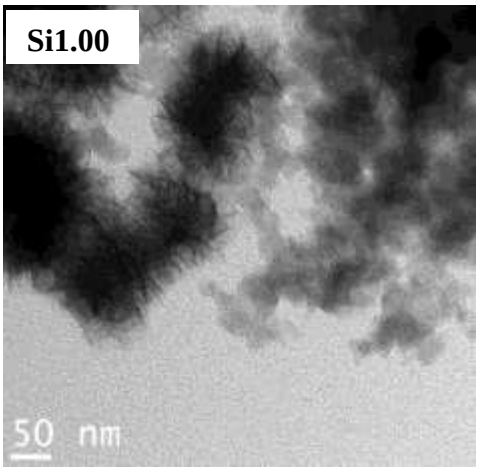

P0.02
50 nm


P0.05
50 nm


P0.20
50 nm


P0.50
50 nm


Si0.20
50 nm


Si1.00
50 nm

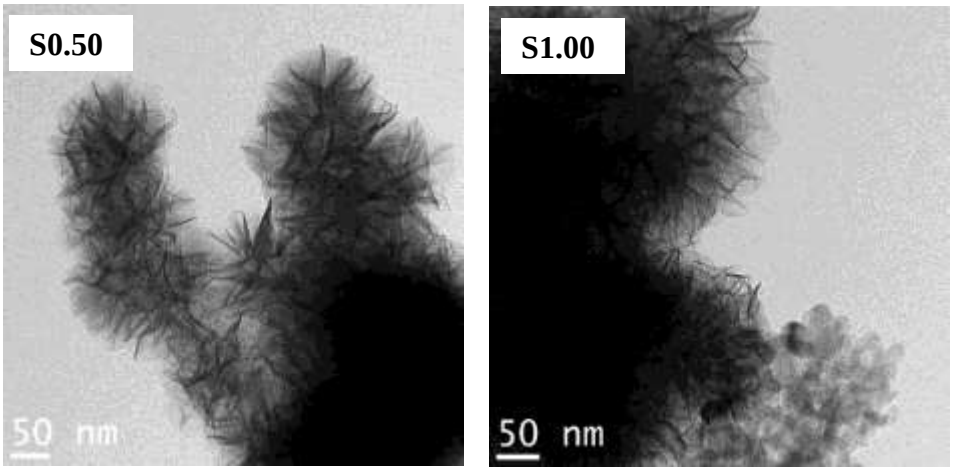


Figure S13. HR-TEM images of some birnessite products.

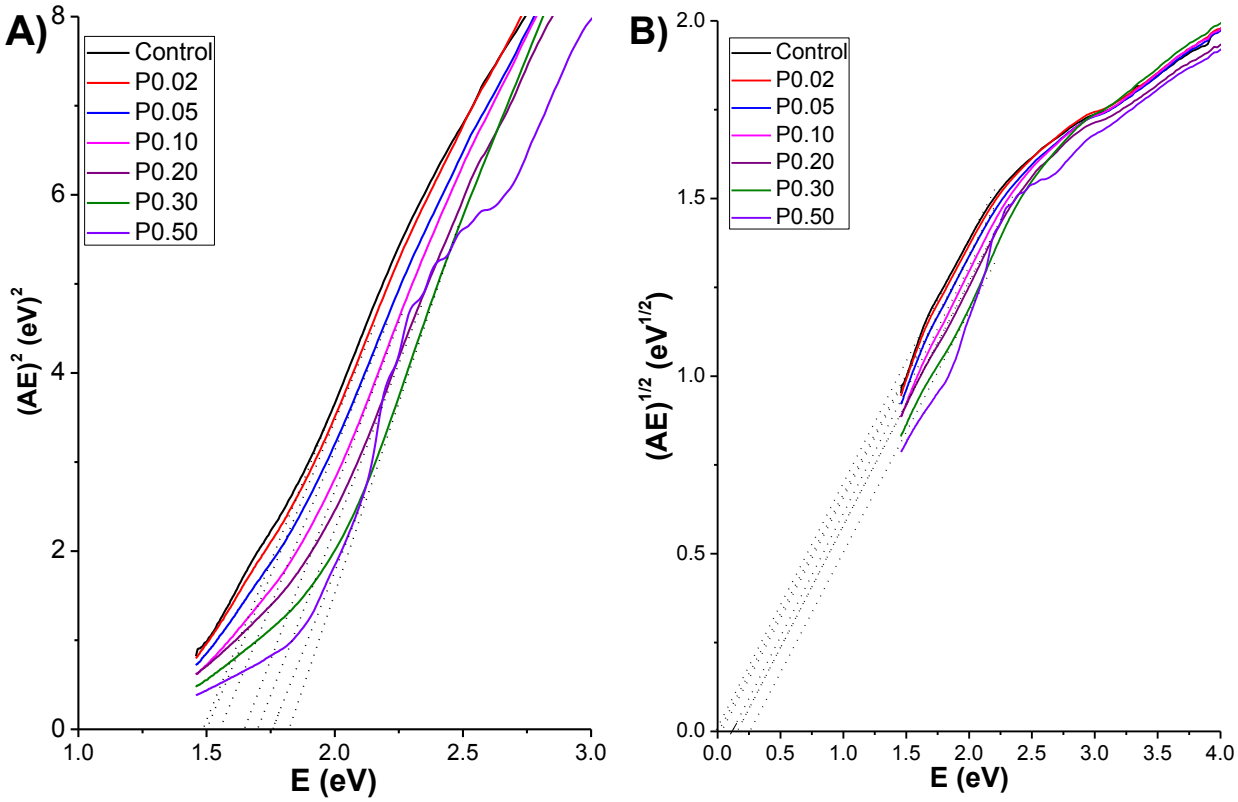


Figure S14. Tauc-Mott plots for determining the direct (A) and indirect (B) band gaps of the P series samples.

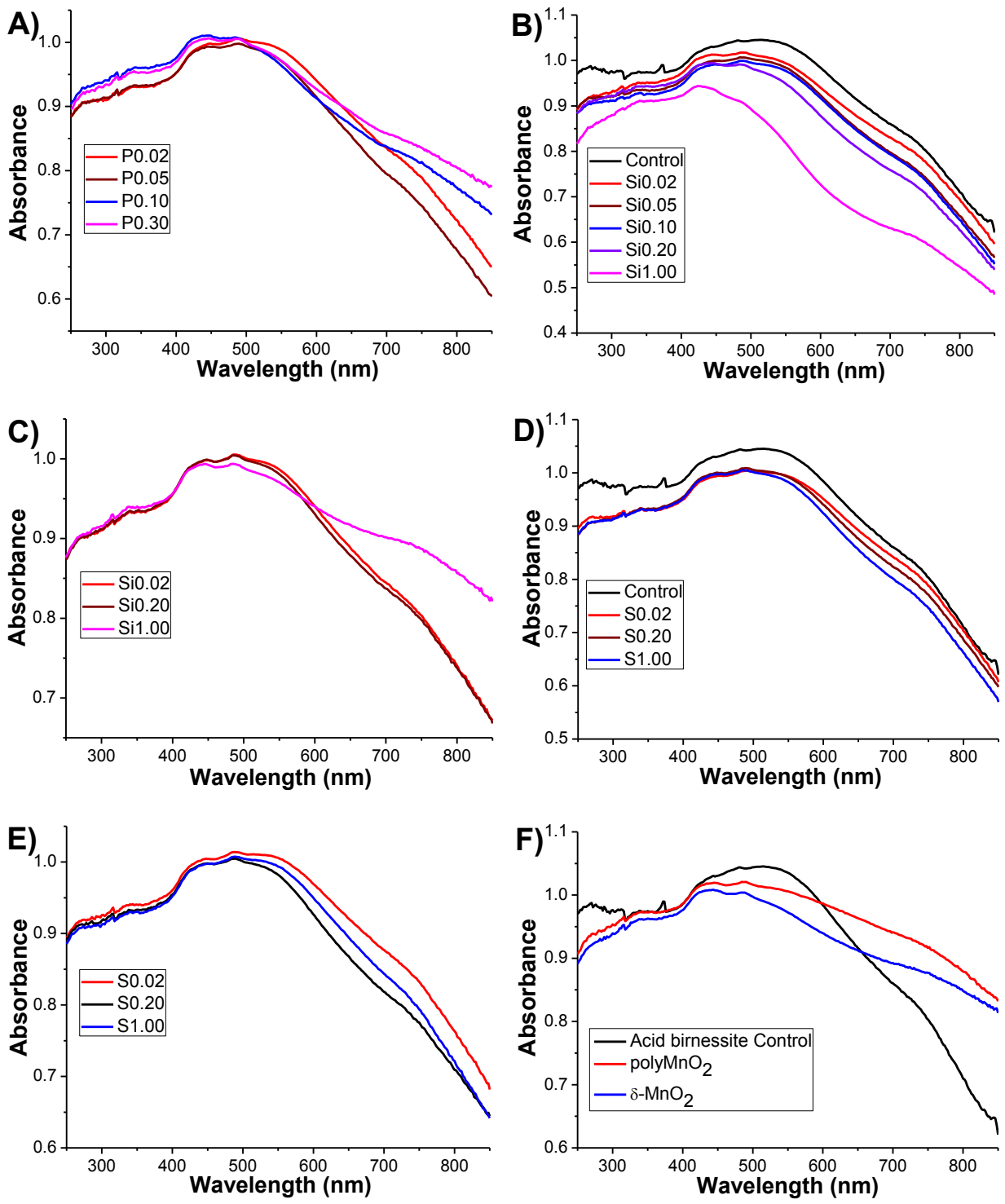
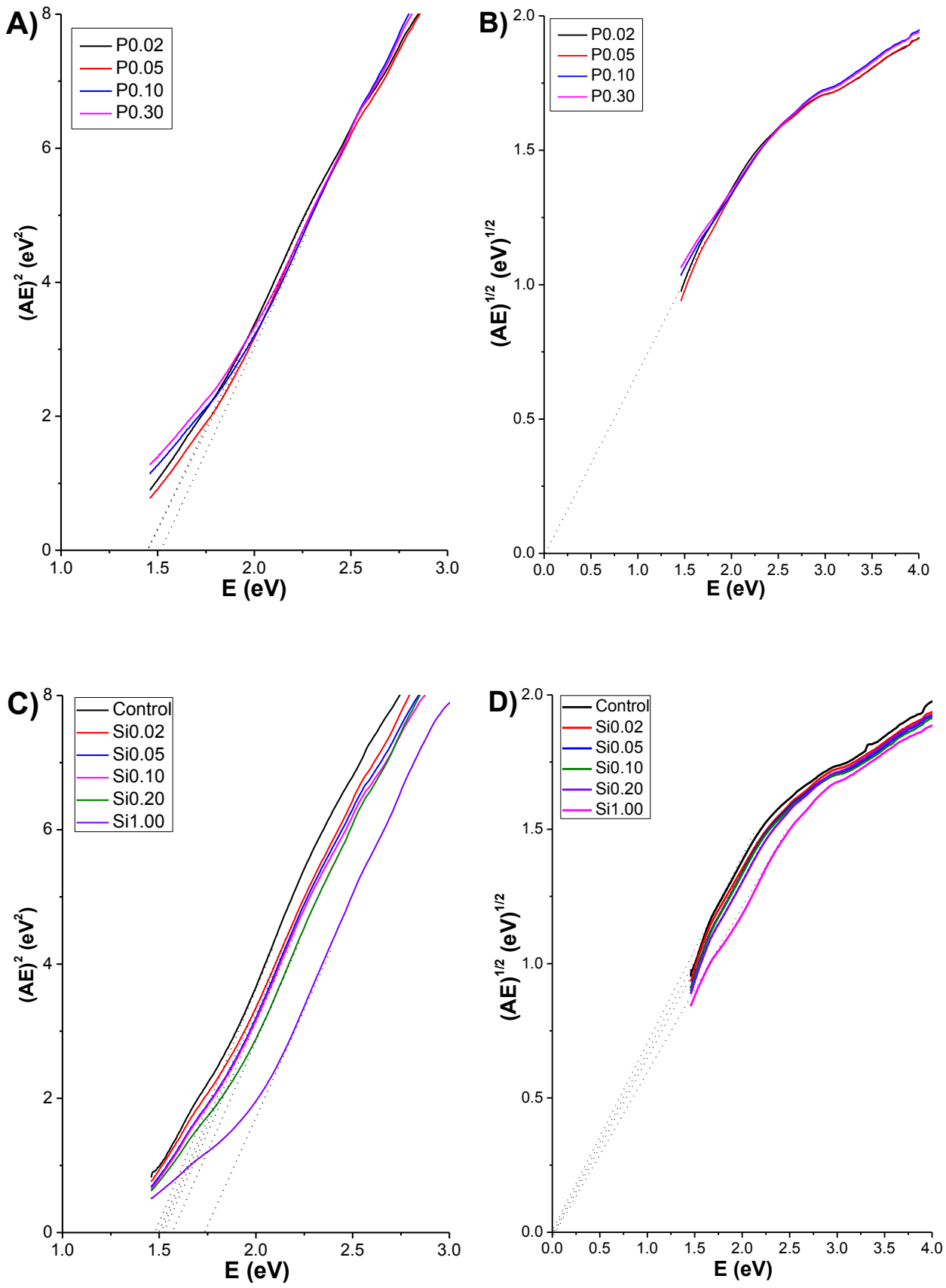
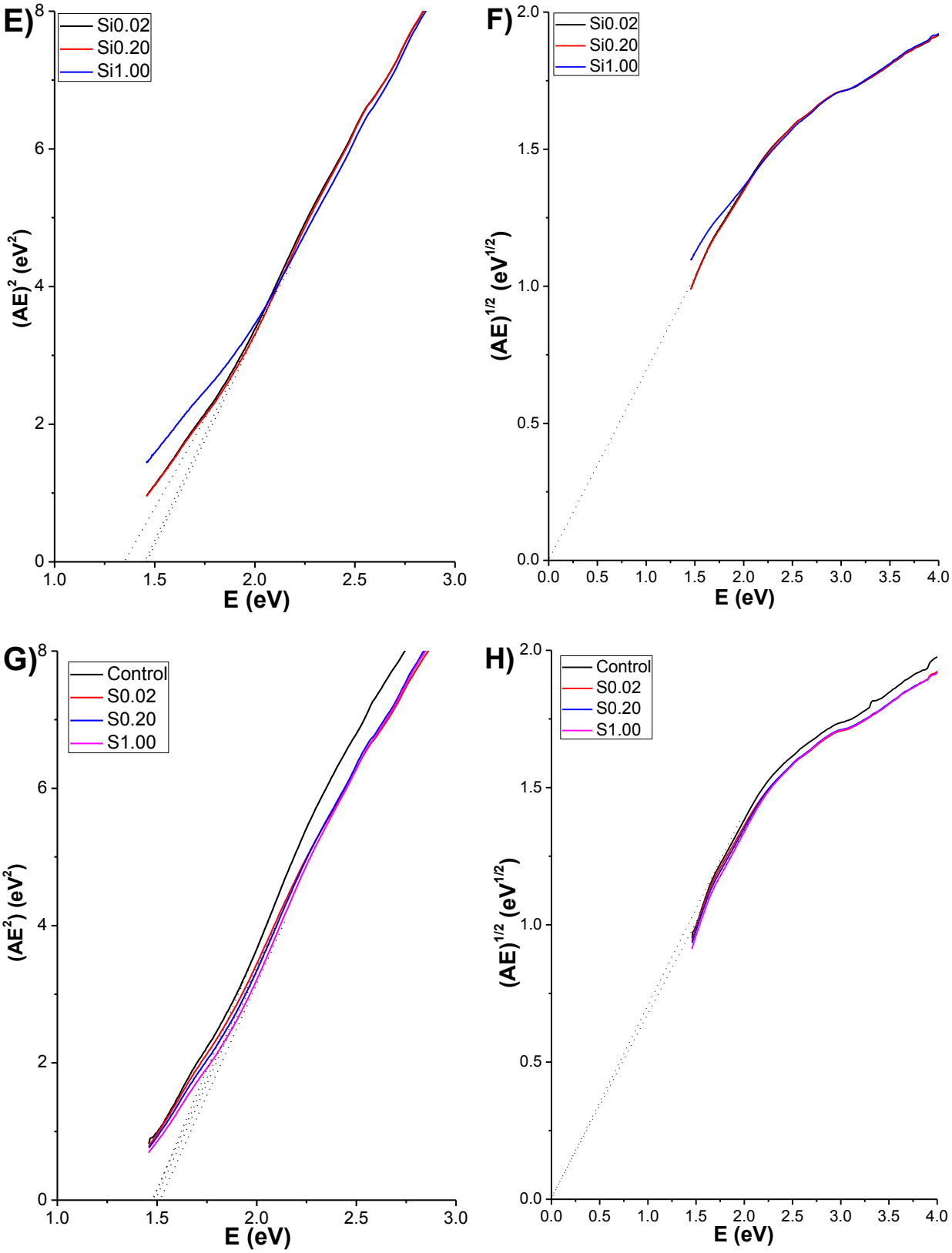


Figure S15. Diffuse reflectance UV-vis spectra of the P series samples washed by 1 M KOH (A), the Si series samples (B), the Si series samples washed by 1 M KOH (C), the S series samples (D), the S series samples washed by 1 M KOH (E), polyMnO$_2$ and δ-MnO$_2$ (F).


A)
P0.02
P0.05
P0.10
P0.30
(AE)^2 (eV^2)
E (eV)
B)
P0.02
P0.05
P0.10
P0.30
(AE)$^{1/2}$ (eV)$^{1/2}$
E (eV)
C)
Control
Si0.02
Si0.05
Si0.10
Si0.20
Si1.00
(AE)^2 (eV^2)
E (eV)
D)
Control
Si0.02
Si0.05
Si0.10
Si0.20
Si1.00
(AE)$^{1/2}$ (eV)$^{1/2}$
E (eV)


E)
Si0.02
Si0.20
Si1.00
(AE)^2 (eV^2)
E (eV)
F)
Si0.02
Si0.20
Si1.00
(AE)$^{1/2}$ (eV$^{1/2}$)
E (eV)
G)
Control
S0.02
S0.20
S1.00
(AE^2) (eV^2)
E (eV)
H)
Control
S0.02
S0.20
S1.00
(AE)$^{1/2}$ (eV$^{1/2}$)
E (eV)

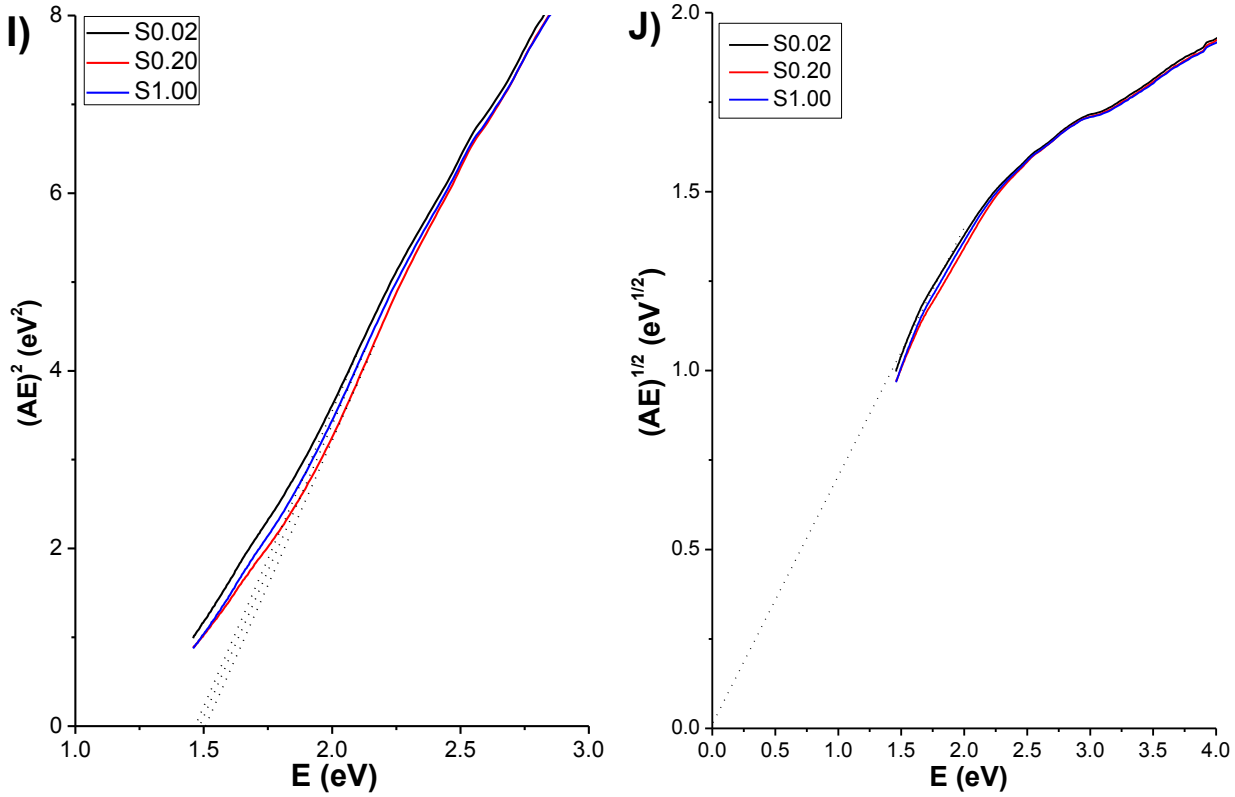


Figure S16. Tauc-Mott plots for determining the direct and indirect band gaps of the P series samples washed by 1 M KOH (A and B), the Si series samples (C and D), the Si series samples washed by 1 M KOH (E and F), the S series samples (G and H), and the S series samples washed by 1 M KOH (I and J).

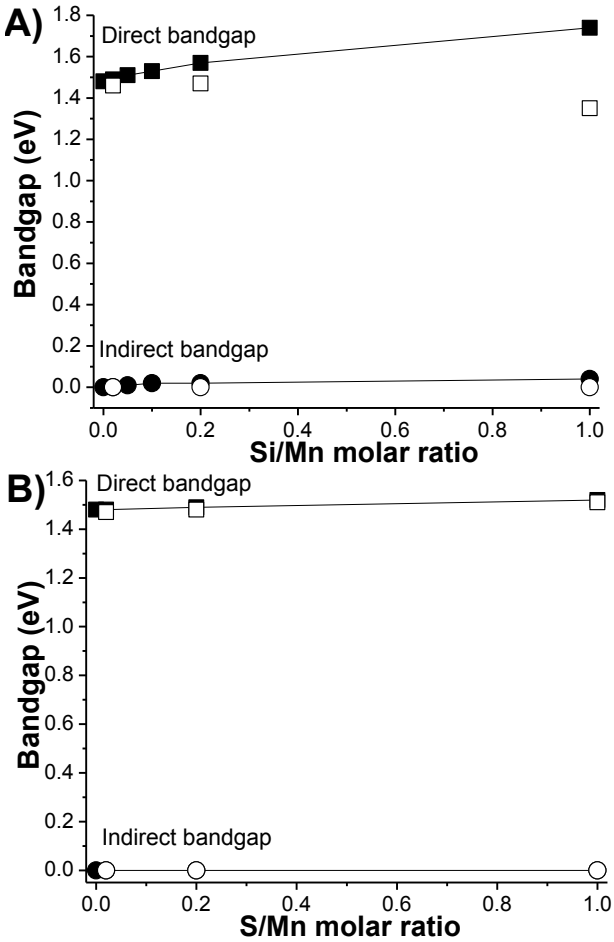


Figure S17. The direct and indirect band gap of Si (A) and S (B) series samples (■: direct band gap; ●: indirect band gap) and those of the corresponding KOH-washed products (□: direct band gap; ○: indirect band gap).

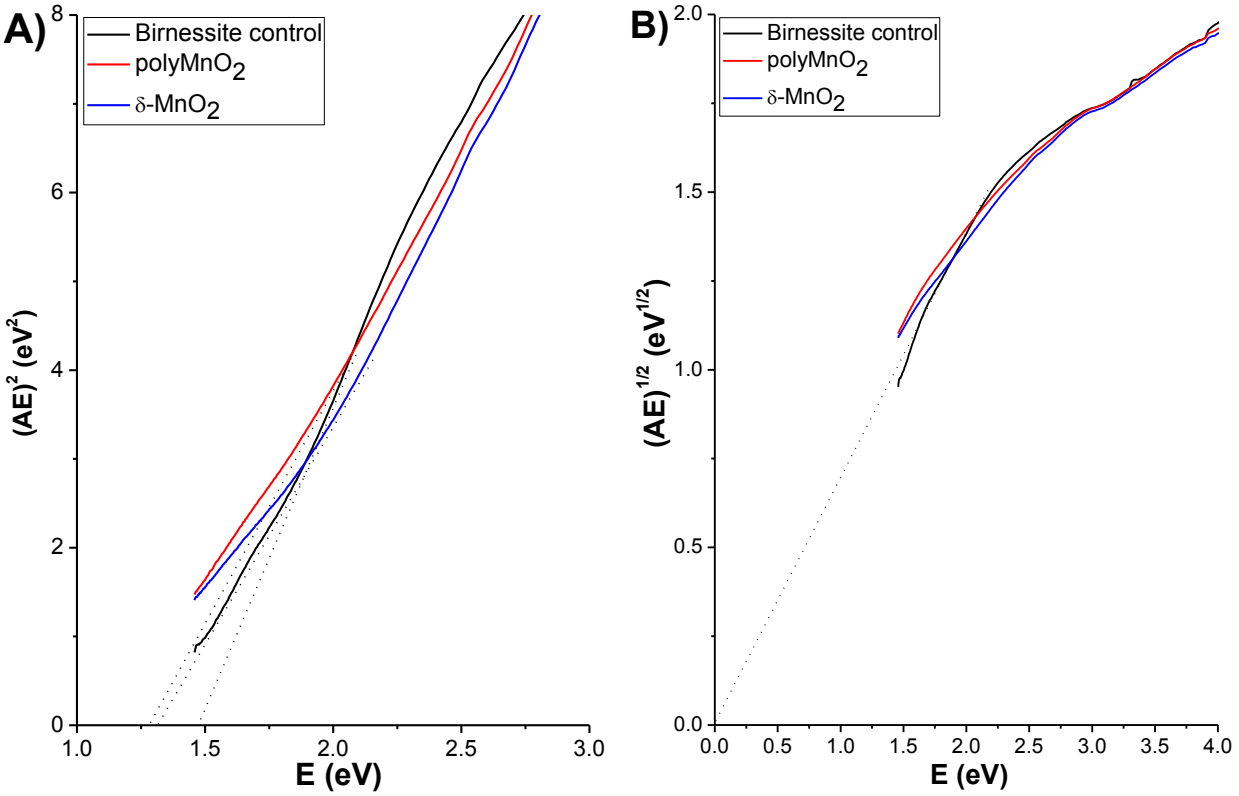


Figure S18. Tauc-Mott plots for determining the direct (A) and indirect (B) band gaps of polyMnO$_2$ and δ-MnO$_2$.