Supplementary Material (ESI) for Journal of Materials Chemistry

Selective Heterogeneous Oriented Attachment of Manganese Oxide Nanorods in Water: Toward 3D Nanoarchitectures

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SUPPORTING INFORMATION

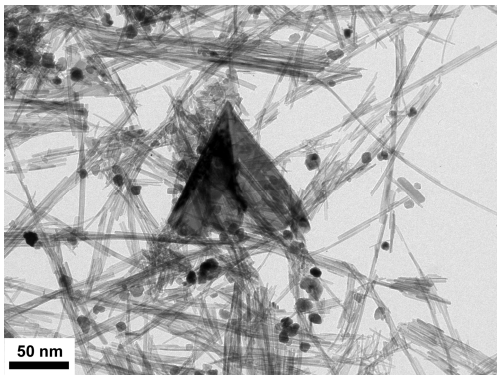


Figure SI-1. TEM image of the sample obtained with the "iso-pH 10" method. The picture is representative of the mixture that is composing the sample: nanorods of manganite γ-MnOOH, platelet-like particles of feitknechtite β-MnOOH, and some spherical particles, characteristic of the hausmannite Mn_3O_4 phase which is usually obtained as minor phase at high evolution pH (pH_f = 10.5).

MUSIC Model calculations

The Brown and Altermatt[52,53] model was used to evaluate the charge burried by the different surface groups. The approximation of the Effective Valence s_{Me} for a metal-oxygen bond was used:

$$s_{Me} = \exp((r_o - r)/B)$$

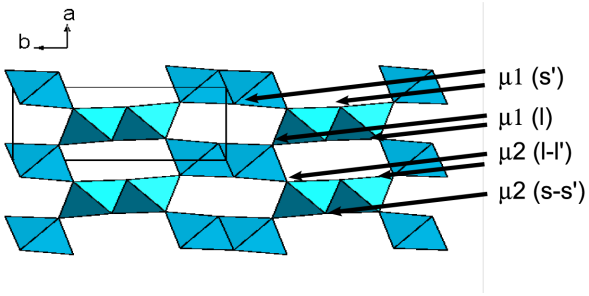
with r the bond length, r_o = 0.179 nm, B = 0.037 nm. The total number of hydrogen atoms linked to a surface oxygen, including covalently bonded and hydrogen bonded H has been fixed to 2 in order to obtain a good agreement with the experimental value of the the isoelectric point evaluated by zetapotential measurements.

The different surface groups taken into account and their calculated characteristics are listed below.

A) Ramsdellite, *R*-MnO_2

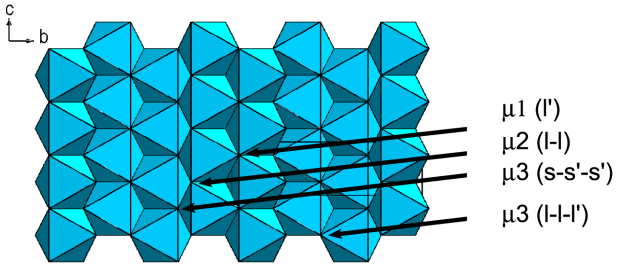
Bond	Length (nm)	Effective Valence
Short (s)	0.182	0.935
Short' (s')	0.190	0.751
Long (l)	0.194	0.660
Long' (l')	0.197	0.610

1) Face (001)



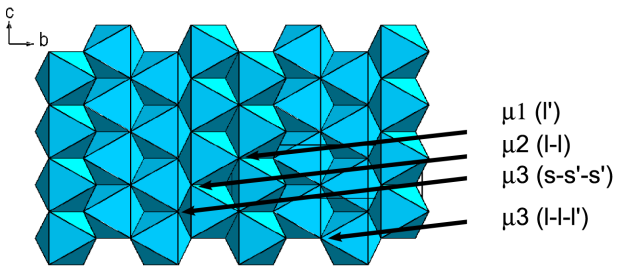
Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	s'	4.82	16.8	4.93	0.75	-0.25	-
μ_1	l	4.82	18.6	6.73	0.66	-0.34	-
μ_2	s-s'	4.82	-1.70	-13.6	-		-0.31
μ_2	l-l'	4.82	6.53	-5.35	-	0.27	-0.73

2) Face (100)



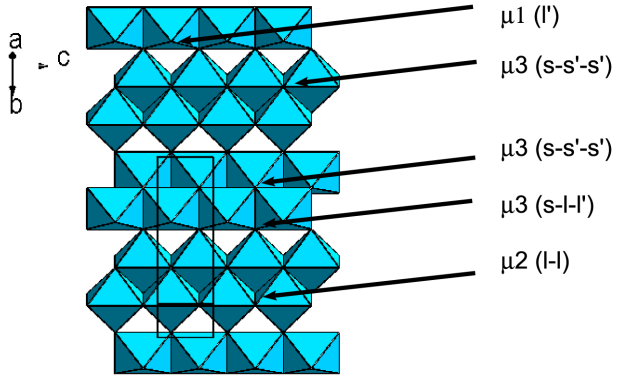
Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	l'	3.77	19.6	7.72	0.61	-0.39	-
μ_2	l-l	3.77	5.54	-6.34	-	0.32	-0.68
μ_3	s-s'-s'	3.77	-12.6	-	-	-	0.44
μ_3	l-l-l'	7.53	-2.57	-	-	-	-0.07

3) Face (010)



Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	s	7.88	13.2	1.29	0.93	-0.07	-1.27
μ_2	s'-s'	7.88	1.94	-9.94	-	-	-0.50
μ_3	l-l-l'	15.77	-2.57	-	-	-	-0.07

4) Face (110), equivalent to (-110)

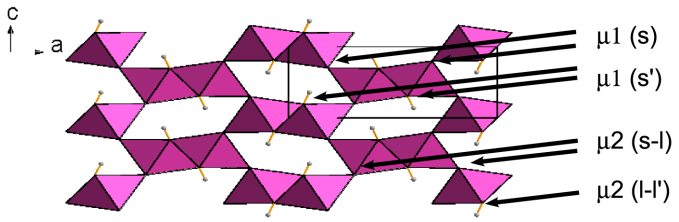


Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	l	3.40	19.6	7.72	0.69	-0.39	-
μ_2	l-l	3.40	5.54	-6.34	-	0.32	-0.68
μ_3	s-s'-s'	6.80	-12.6	-	-	-	0.44
μ_3	l-l-l'	6.80	-2.57	-	-	-	-0.07

B) Groutite, α-MnOOH

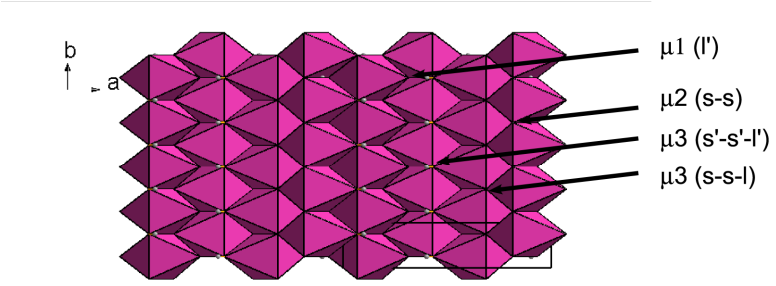
Bond	Length (nm)	Effective Valence
Short (s)	0.189	0.755
Short' (s')	0.197	0.623
Long (l)	0.217	0.354
Long' (l')	0.234	0.227

1) Face (010)



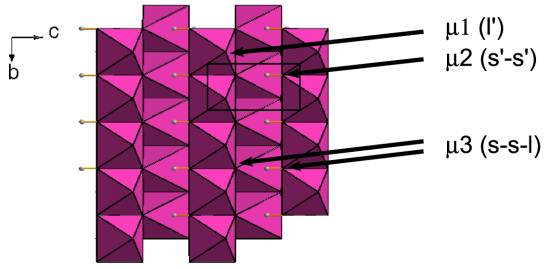
Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	s	4.12	16.7	4.85	0.76	-0.25	-
μ_1	s'	4.12	24.1	7.46	0.62	-0.38	-
μ_2	s-l	4.12	9.72	-2.15	-	0.11	-0.89
μ_2	s'-l'	4.12	14.9	2.97	0.85	-0.15	-1.15

2) Face (001)



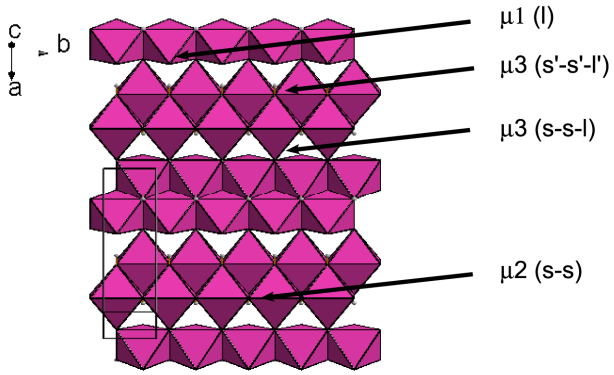
Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	s	3.27	16.7	4.85	0.76	-0.25	-
μ_2	s-s	3.27	1.78	-10.1	-	0.51	-0.49
μ_3	s-s-l	3.27	-13.1	-	-	-	-0.14
μ_3	s'-s'-l'	6.53	6.47	-5.41	-	0.47	-0.53

3) Face (100)



Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	s	7.65	27.2	15.3	0.23	-0.77	-
μ_2	s-s	7.65	7.01	-4.87	-	0.25	-0.75
μ_3	s-s-l	15.3	-13.1	-	-	-	-0.14

4) Face (101)



Surface group	Bond	Density (nm^{-2})	pK_A (OH/O)	pK_A (OH_2/OH)	OH_2 charge	OH charge	O charge
μ_1	l	3.00	24.7	12.8	0.35	-0.65	-
μ_2	s-s	3.00	1.78	-10.1	-	0.51	-0.49
μ_3	s-s-l	6.00	-13.1	-	-	-	-0.14
μ_3	s'-s'-l'	6.00	6.47	-5.41	-	0.47	-0.53