Supplementary Material (ESI) for Chemical Communications

Supporting Information

Nanostructured Manganese Oxide Clusters Supported on Mesoporous Silica as Efficient Oxygen-Evolving Catalysts

Feng Jiao and Heinz Frei*

Physical Biosciences Division, Lawrence Berkeley National Laboratory,

University of California, Berkeley, CA 94720

Experiment section

Synthesis of KIT-6/MnO_x:

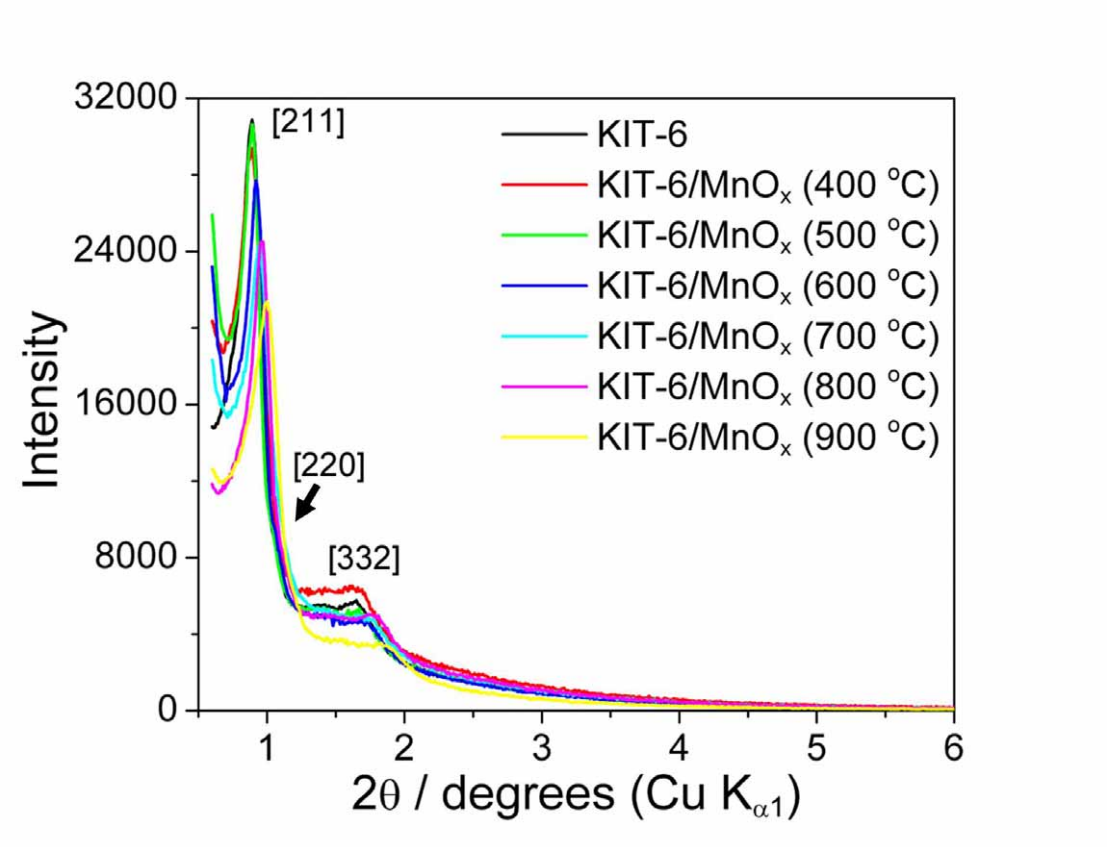
Preparation of mesoporous silica KIT-6 and bi-solvent method have been described previously [1-3]. The structural parameters of KIT-6 are reported in Ref. [4]. In a typical synthesis of KIT-6/MnO_x, $Mn(NO_3)_2{\cdot}6H_2O$ (98%, Aldrich) was dissolved in 2 mL of water to form a $Mn(NO_3)_2$ aqueous solution. 2 g of mesoporous KIT-6 was dispersed in 100 mL of dried n-hexane. After stirring at room temperature for 30 min, 2 mL of as-made $Mn(NO_3)_2$ solution was added slowly under stirring. The mixture was continuously stirred for 3 h, and then filtered and dried at room temperature until a completely dried powder was obtained. The sample was heated slowly to 400-900 ^oC and calcined at that temperature for 3 h.

1. F. Kleitz, S.H. Choi, R. Ryoo, *Chem. Commun.,* 2003, 2136.
2. M. Imperor-Clerc, D. Bazin, M.D. Appay, P. Beaunier, A. Davidson, *Chem. Mater.,* 2004**, 16**, 1813.
3. F. Jiao, P.G. Bruce, *Adv. Mater.,* 2007**, 19**, 657.
4. M.R. Hill, S.J. Pas, S.T. Mudie, D.F. Kennedy, A.J. Hill, *J. Mater. Chem.,* 2009, **19**, 2215.

Water oxidation catalysis experiments:

Visible light-driven O_2 evolution in aqueous suspensions of Mn oxide/KIT-6 catalysts was determined by mass spectrometric analysis of the gas in the head space volume. The 40 mL buffered solution (Na_2SiF_6, $NaHCO_3$, 0.022-0.028 M, pH 5.8) contained 130 mg $Na_2S_2O_8$ (electron acceptor), 390 mg Na_2SO_4, 45 mg $([Ru(bpy)_3]Cl_2{\cdot}6H_2O$ (sensitizer), and 200 mg Mn oxide/KIT-6 (8%, containing 12 mg Mn). For experiments with μ-sized Mn oxide particles, 200 mg of MnO_2, Mn_2O_3, or Mn_3O_4 were used. Mildly acidic conditions were used in order to minimize photodegradation of the Ru sensitizer. The catalyst was degassed in a Schlenk tube under

vacuum overnight and refilled with Ar before being transferred into the reaction bulb. Irradiation of the solution at 476 nm (Ar ion laser emission, 240 mW, 1.6 cm diameter beam) resulted in O_2 generation. Oxygen yield versus time plots of Figure 3 were obtained by periodically capturing 2.5 mL gas from the head space followed by injection into a quadrupole mass spectrometer (Pfeiffer model Omnistar 422). For all catalyst samples, the amount of O_2 generated increased close to linearly over the initial 30 min of photolysis but leveled off after about one hour because of consumption of persulfate acceptor. This was confirmed by adding another 130 mg of NaS_2O_8 to the photolysed solution, re-adjusting the pH from 5.08 to 5.80 with $NaHCO_3$ and bubbling Ar for 30 min. to remove any dissolved O_2, and continuing photolysis under identical conditions. Within experimental error of 5%, the same O_2 yield was measured as in the initial run demonstrating the stability of the Mn oxide/KIT-6 catalyst. Recording of the K-edge position by X-ray absorption spectroscopy of the Mn oxide/KIT-6 catalysts before and after photolysis confirmed the integrity of the Mn oxidation state.



.

Parameters of the mesostructure obtained from the [211] reflection PXRD data.

	KIT-6	KIT-6/MnO_x					
		400 °C	500 °C	600 °C	700 °C	800 °C	900 °C
2θ	0.89	0.88	0.89	0.92	0.95	0.96	0.99
d spacing / Angstrom	99	100	99	96	93	92	89
α / Angstrom	243	246	243	235	228	225	218

Figure S1. Low-angle powder X-ray diffraction patterns for KIT-6 and KIT-6/MnO_x.

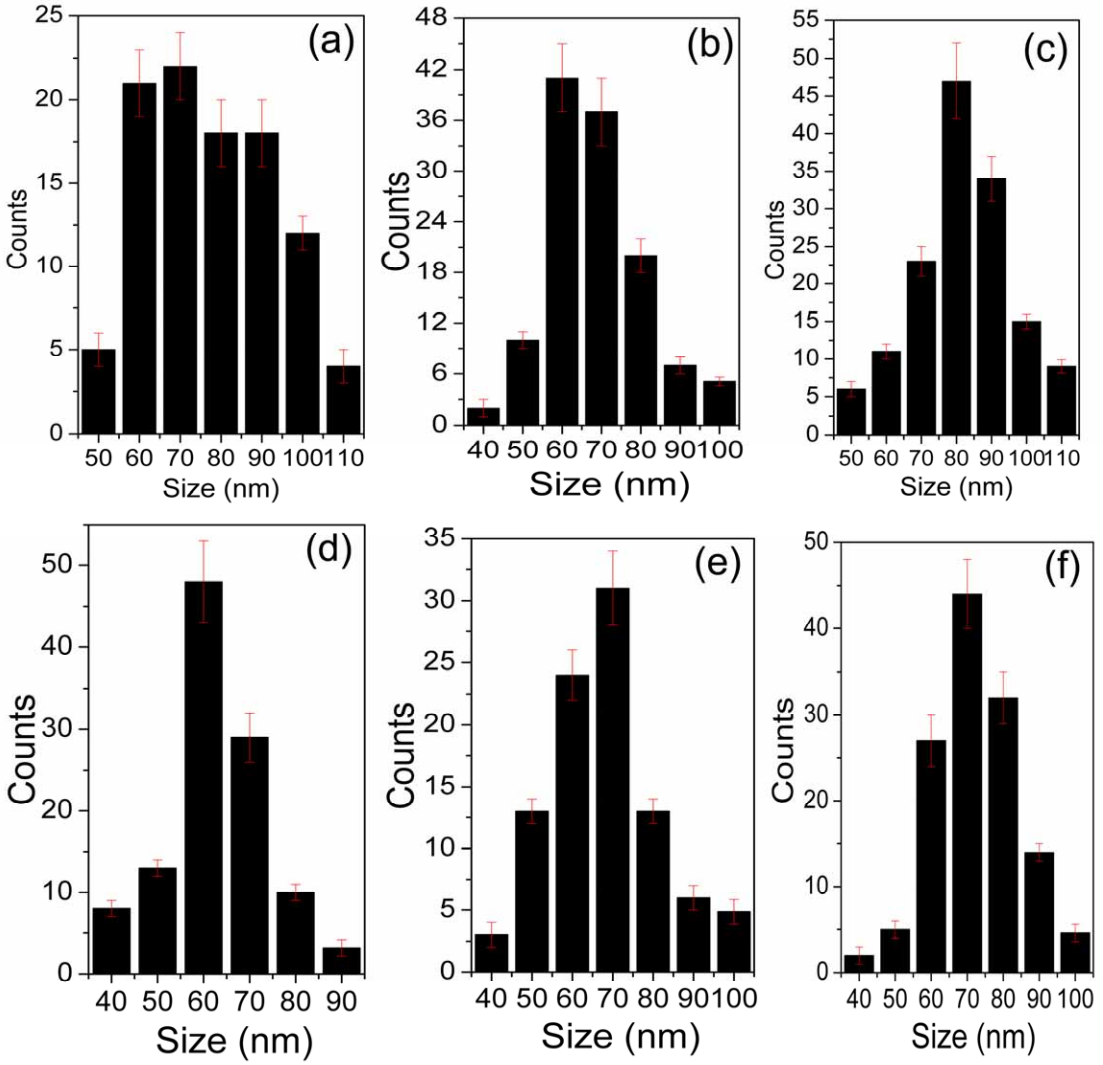


Figure S2. Particle size analysis for Mn oxide nanoclusters supported in mesoporous silica KIT-6 calcined at (a) 400 ^{o}C, (b) 500 ^{o}C, (c) 600 ^{o}C, (d) 700 ^{o}C, (e) 800 ^{o}C, and (f) 900 ^{o}C.

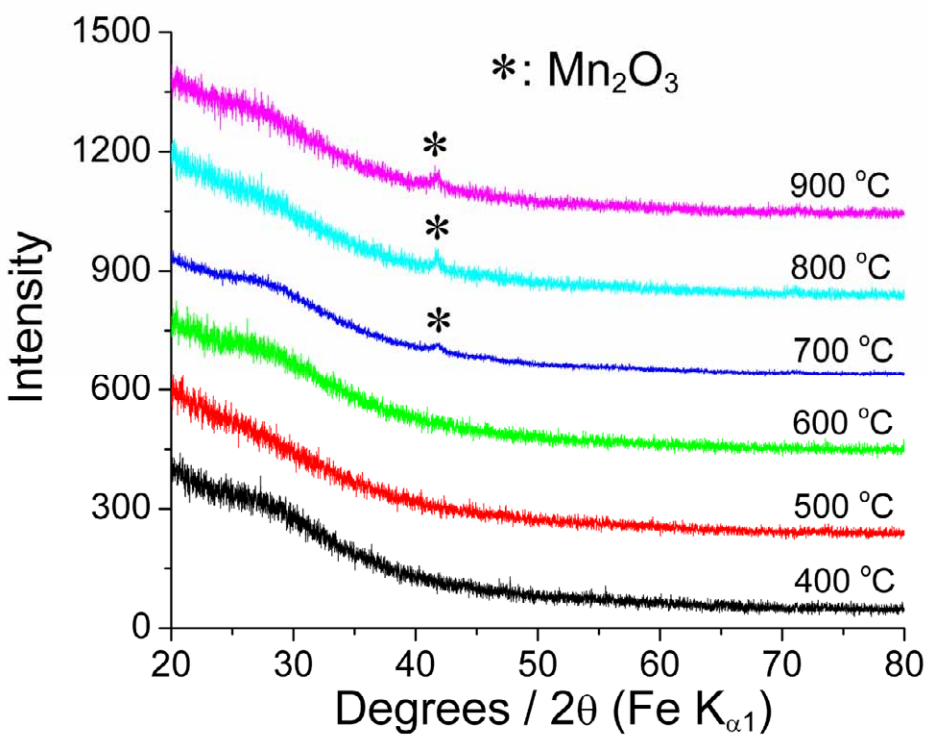


Figure S3. Wide angle PXRD patterns for KIT-6/MnO_x samples calcined at various temperatures.

Calcination temperature / ^{o}C	400	500	600	700	800	900
Mean diameter / nm	82.2	72.9	85.9	66.9	72.9	77.4
Standard deviation	15.9	12.9	14.1	11.6	14.2	12.3

Table S1: Mean diameter and standard deviation of Mn oxide nanoclusters supported on KIT-6.

	MnO_2	Mn_2O_3	Mn_3O_4
400 ^{o}C	64%	36%	0
500 ^{o}C	95%	5%	0
600 ^{o}C	6%	80%	14%
700 ^{o}C	0	81%	19%
800 ^{o}C	0	70%	30%
900 ^{o}C	0	51%	49%

Table S2: Component analysis results for KIT-6/MnOx by least squares fitting function (SIXPACK software, S. Webb, SSRL) showing fractional phase content (wt%).