Supporting Information

Mesoporous Ferrihydrite with Incorporated Manganese for Rapid Removal of Organic Contaminants in Air

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Synthesis of MMnFh

For MMnFh (Mn/Fe mole ratio of 0.5) synthesis, 0.04 mole of $Fe(NO_3)_3.9H_2O$ and 0.02 mole of $Mn(NO_3)_2.6H_2O$ were added to a clear solution of 34.04 g polyoxyethylene (20) cetyl ether (Brij 58) in 300 ml 1-propanol at room temperature (RT). Precipitation was carried out by adding 28% NH_3 solution to the above solution to a pH of ~ 7.5-8, followed by stirring for 3 h and ageing at 50°C in a closed vessel for 3 days. The solid mass was filtered, washed with ~2.0-2.5 L water, and finally dried. About 3 g of the dried powder was then stirred with 100 ml ethanol at RT for 24 hours, filtered, washed with water, dried and finally calcined at 300°C for 3 h.

Experimental details of organic contaminant elimination

The organic contaminat elmination experiment was carried out in static condition. Briefly, a gas mixture comprised of 31.7 ppm CH_3CHO or (31.7 ppm CH3CHO + 20 ppm toluene), 20% O_2, and the balance of N_2, and 0.1 g or (0.3 g) sample were introduced in a 5 L container made of polyvinyl fluoride. As shown in Figure S1, each gas from a separately procured gas cylinder was used for the experiments. The gas mixture was introduced to the container through a gas mixing chamber and a flow meter. The gas container was then kept in a chamber that maintained at a desired temperature of interest, such as 25°C or 80°C in the present study. The concentration of the gas remained in the container was measured by a GC at various intervals of time. We conducted separate experiments that didn't use any catalyst in the container (which is called blank tests). The percentage removal of Volatile organic compound (VOC) was calculated according to the equation: % VOC removal = [1 – (concentration of VOC with catalyst/concentration of VOC without catalyst)]*100. The reproducibility of the result was confirmed by repeating the experiments for the best performing catalysts.

To check the CO_2 formation, about 0.1 g catalyst material and 1000 ppm CH_3CHO containing air mixture were used (0.5 L bottle). Several blank tests were also performed and the CO_2 formation was calculated with respect to blank. CO_2 analysis was conducted in a separate GC equipped with a methanizer.

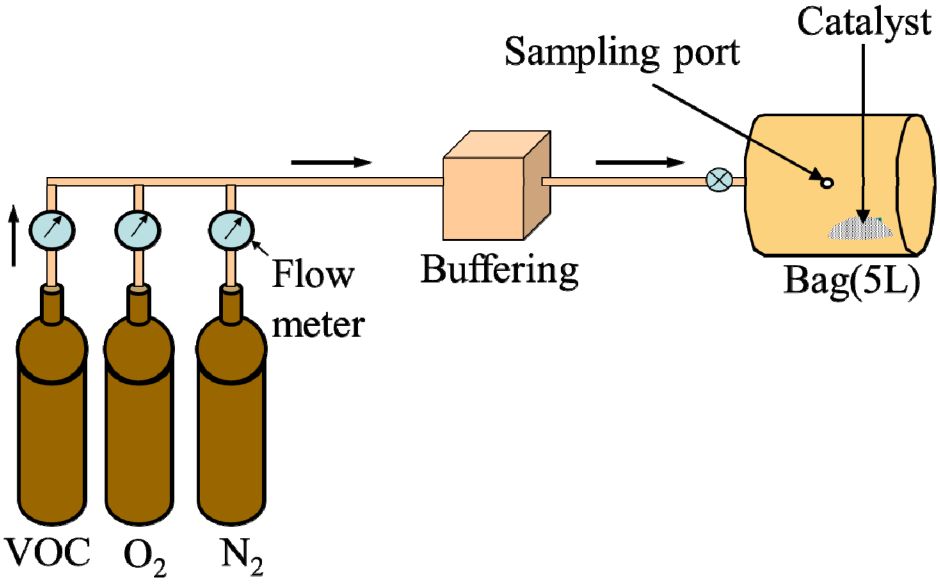

Figure S1: A schematic diagram of the experimental design for organic contaminant elimination.

Experimental details of various Characterization

XRD patterns were obtained on a Rigaku Rint-2400 instrument using Cu Kα radiation operating at 40 kV and 30 mA. TEM observations were made with a JEM200CX instrument (Hitachi) at an accelerating voltage of 200 kV. N_2 adsorption analysis was carried out on a BELSORP 18 apparatus (BEL Japan, INC). The XPS measurements were carried out on a Quantera SXM (Ulvac-PHI) spectrometer using Al *Kα* X-ray radiation (hν = 1486.6 eV).

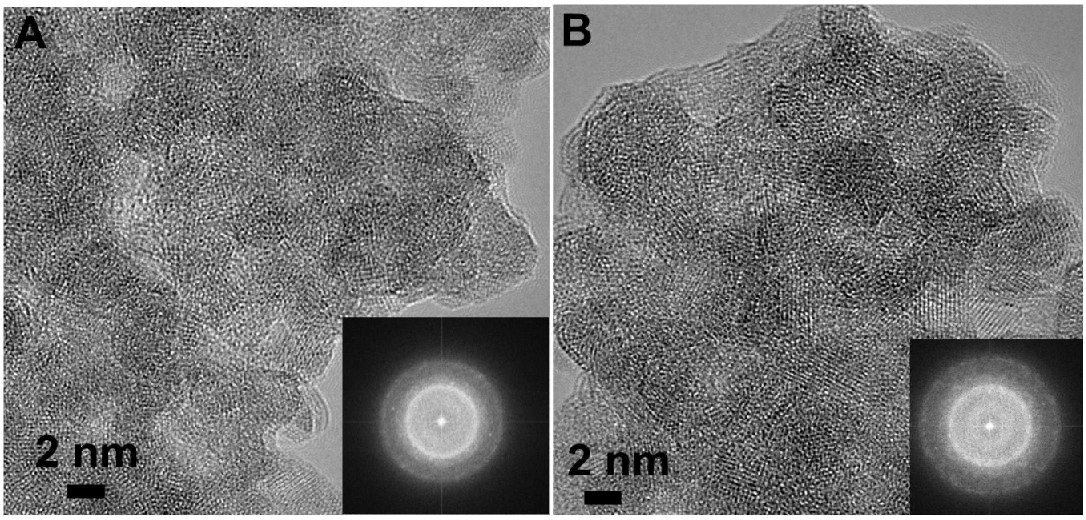

Figure S2: HRTEM images of (A) ethanol extracted as-synthesized, and (B) calcined (at 300°C) samples of MMnFh (Mn/Fe mole ratio = 0.5). The corresponding fast Fourier transform (FFT) diffraction is shown in the inset for each case.

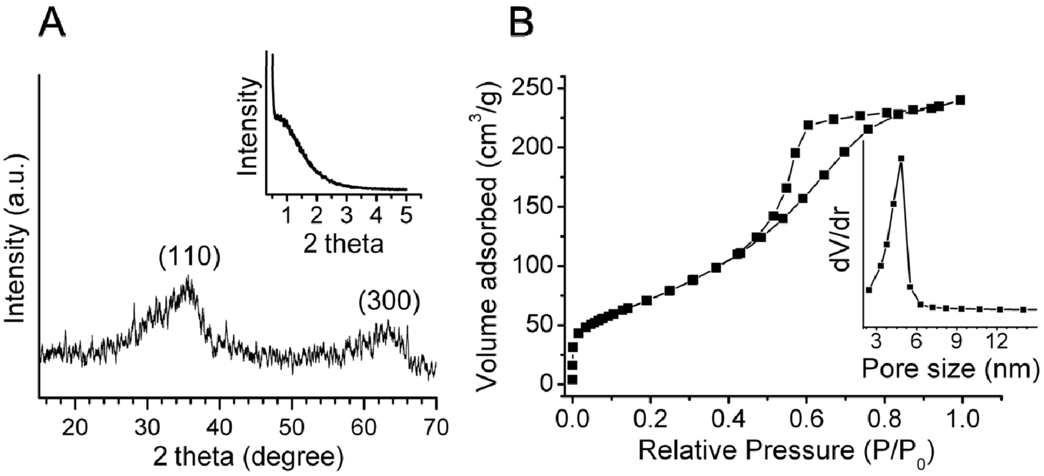

Figure S3: (A) XRD pattern (low angle XRD is in inset) of MMnFh obtained after calcination at 400°C, which illustrates that MMnFh remains in Fh phase. (B) Nitrogen adsorption-desorption isotherms of MMnFh calcined at 400°C. The Barrett-Joyner-Halenda (BJH) analysis of pore size distribution is given in the inset. The porosity parameters of MMnFh after calcination at 400°C are BET surface area: 286 m^2g^{-1}, pore size: 4.8 nm, and pore volume: 0.40 cm^3g^{-1}.

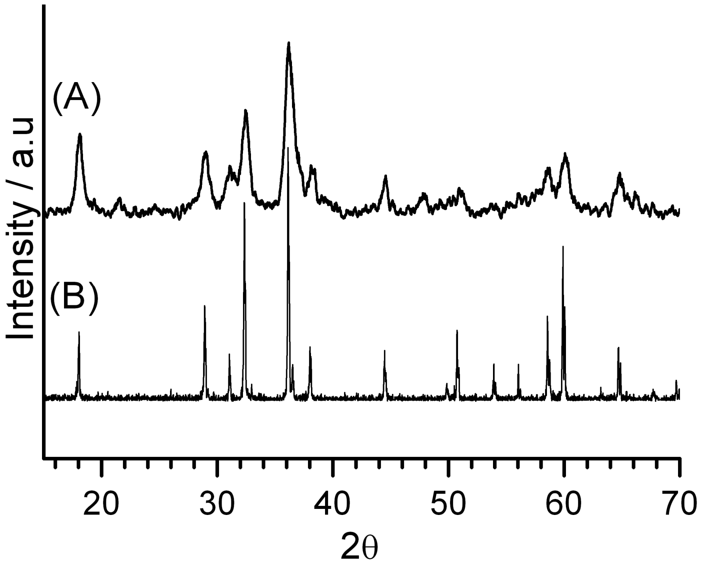

Figure S4: (A) XRD pattern of the material obtained after calcination at 300°C when $Mn(NO_3)_2$ alone was used for the synthesis. The synthesis was carried out under similar experimental conditions described for synthesizing MMnFh, where the nitrate salts of both iron and manganese were used for the synthesis. Note that the XRD pattern of the product is characteristic of Mn_3O_4. (B) XRD pattern of a standard sample of Mn_3O_4 (proclaimed from Aldrich) is shown for comparison.

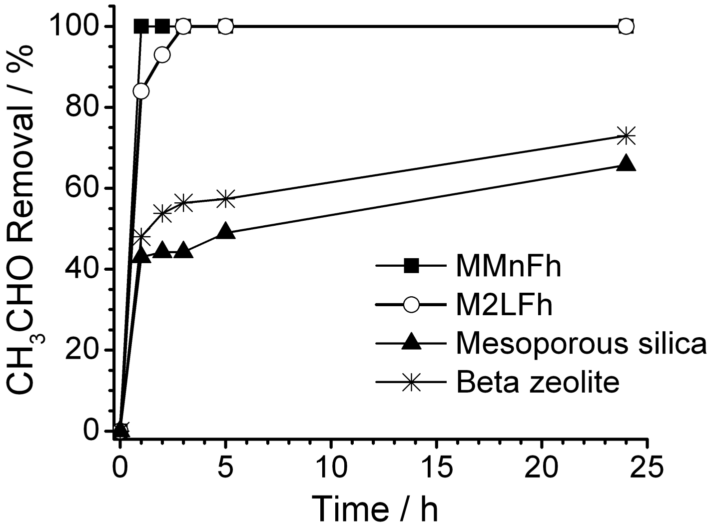

Figure S5: The time-dependent CH_3CHO removal efficiency of various materials at room temperature ((31.7 ppm CH_3CHO, 5L, 0.1 g sample).

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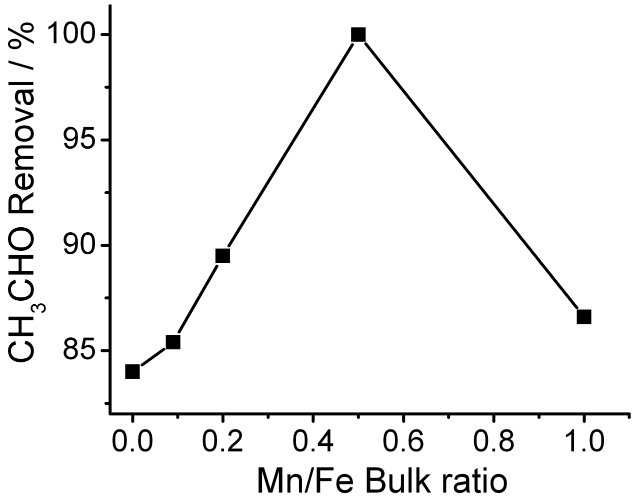

Figure S6: The first hour of CH_3CHO removal efficiency of MMnFh nanoparticles as a function of Mn/Fe mole ratio at room temperature ((31.7 ppm CH_3CHO, 5L, 0.1 g sample).

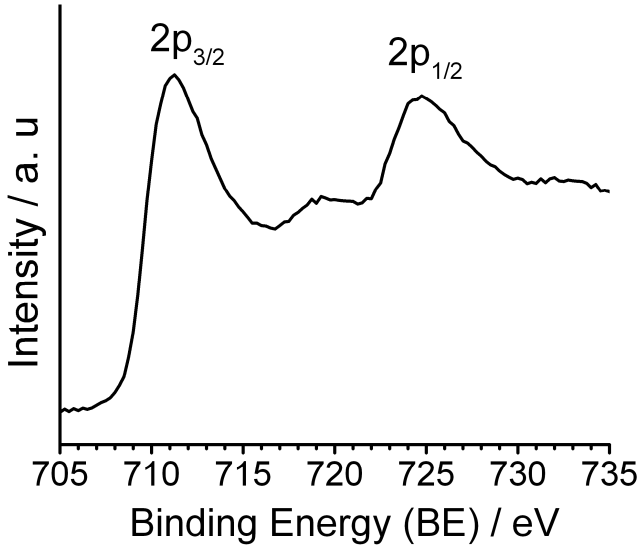

Figure S7: Fe 2p core level XPS spectrum of MMnFh (obtained after calcination at 300°C).

Computational Details for ferrihydrite surface structure calculation

All calculations were carried out using density functional theory (DFT) with PWscf code.[1] Exchange correlation was treated in the generalized gradient approximation (GGA) with Perdew Burk, and Ernzerhof (PBE).[2] The pseudo potentials were $3d^5 4s^2$ for Mn, $3d^7 4s^1$ for Fe, $2s^2 2p^4$ for O, and $1s^1$ for H. We also utilized GGA+U method in order to modify GGA energies with an explicit correction for the Coulomb interaction of the 3*d* electrons of Fe and Mn.[3] The Hubbard U parameter was set to 4eV (Ueff = $3eV$). The U value was utilized by Pinney *et al.* and Rollman *et al.*[4,5] The geometry optimization of bulk structure was performed with a 4 × 4 × 3 Monkhorst Pack **k**-point grid and a plane wave kinetic cutoff energy of 30Ry. The (110) surface structural optimization was performed with a 2 × 2 × 1 Monkhorst Pack **k**-point grid and a planewave kinetic cutoff energy of 30Ry. Our results are in close agreement with the previous studies (Table S1). The optimized bulk model of Mn-Fh used for surface structure calculation was the most stable among 120 different combinations of Mn substitutions in the DFT optimized bulk Fh structure that we performed. The DFT optimized bulk structure and unit cell parameters for simple Fh and Mn-Fh are compared in Figure S7 and Table S1. For surface structure calculation, the most exposed (110) surface cluster was generated from the DFT optimized bulk structure of Fh or Mn-Fh. Subsequently, geometry optimization of (110) surface was performed by keeping the bottom layer of the (110) cluster atoms to a fixed position.

Reference for this section

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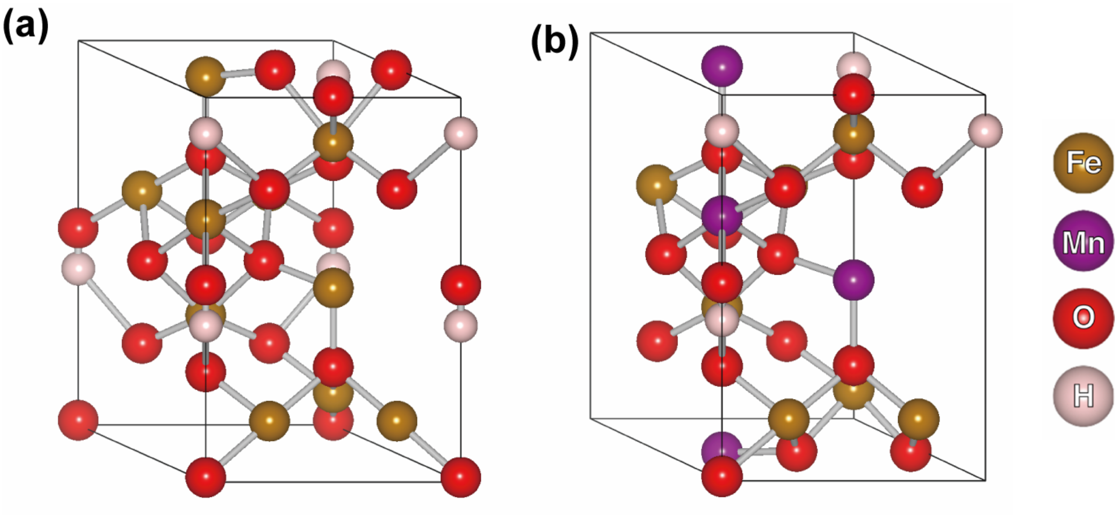

Figure S8: DFT optimized bulk structure of (a) Ferrihydrite and (b) Mn incorporated Ferrihydrite.

Table S1: Comparison of the experimental and theoretically calculated (DFT GGA + *U* method) unit cell dimensions of Ferrihydrite (Fe_5O_8H, space group: $P6_3mc$) and Mn incorporated Ferrihydrite.

Material	[a]**Unit cell dimensions**			**Reference**
	***a*, Å**	***b*, Å**	***c*, Å**	
Mn-Ferrihydrite	6.08	6.08	9.22	DFT method (present work)
Ferrihydrite	6.00(1.2 %)	6.00 (1.2 %)	9.36 (2.5 %)	DFT method (Mathew et al *Chem. Eur.J.,* in press)
Ferrihydrite	5.99 (1%)	5.99 (1%)	9.35 (2.4%)	DFT method (N. Pinney et al *Chem. Mater.* **2009**, *21*, 5727)
Ferrihydrite	5.93	5.93	9.13	Experimental (F. M. Michel et al *Science* **2007**, *316*, 1726)

[a] The value given in the parenthesis of unit cell dimensions for theoretical (DFT GGA + *U*) cases indicate the percentage error in unit cell dimensions with respect to the experimentally determined values of unit cell dimensions (F. M. Michel et al *Science* **2007**, *316*, 1726).