Supporting Information

Aggregated manganese complex-nanolayered manganese oxide: A new hybrid molecularinorganic material

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Experimental Section

Materials

All reagents and solvents were obtained from commercial sources and used without further purification, unless otherwise stated. 2,4,6-tris(2-pyridyl)-1,3,5-triazine, manganese(II) chloride, manganese(II) acetate, H_2O_2 , and tetramethylammonium hydroxide were purchased from Merck Company. For the experiments, milli-Q water (18-20 M Ω •cm⁻¹ at 27 °C) was used.

Characterization

SEM was carried out using an LEO 1430VP microscope. HRTEM and TEM were carried out using an FEI Tecnai G² F20 transmission electron microscope, TF20 (200 kV). The X-ray powder diffraction patterns were recorded with a Bruker D8 Advance (Germany) diffractometer (CuK_{α} radiation).

X-ray Photoelectron Spectroscopy (XPS, K-ALPHA, Thermo Scientific) was used to analyze the sample surfaces. All spectra were collected using Al-K radiation (1486.6 eV), monochromatized by a twin crystal monochromator, yielding a focused X-ray spot at 3 mA × 12 kV. The alpha hemispherical analyzer was operated in the constant energy mode with survey scan pass energies of 200 eV to measure the whole energy band and 50 eV in a narrow scan to selectively measure the particular elements. XPS data were analyzed with Avantage software. A smart background function was used to estimate the experimental backgrounds, and surface elemental compositions were calculated from background-subtracted peak areas. Charge compensation was achieved with the system flood gun that provided low energy electrons and low energy argon ions from a single source. The penetration depth was around 3 nm. FTIR spectra of the materials prepared as KBr pellets were recorded on a Bruker vector 22 in the range between 400 and 4000 cm⁻¹. Magnetic properties were investigated using a Quantum Design MPMS-XL-5 magnetometer (compound 1 (48.40 mg); complex 1 (8.32 mg); compound 2 (12.92 mg)). The EPR measurements were carried out using a Bruker EMX spectrometer working at a fixed frequency of 9.25 GHz (X-band). A 100 kHz magnetic field modulation and phase-sensitive detection were used to record the derivative of the absorbed microwave power. The amplitude of absorption was normalized by the mass of samples to compare different samples. UV-Vis spectra for solid state materials and materials in solution were performed UV-Vis-NIR spectrophotometer (Varian, Model: Cary 5E) and Pharmacia Biotech ultrospec 3100, respectively.



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Figure S1 The phase conversation and XRD patterns for layered Mn oxide after ten hours under the reported temperature; At 400-600 °C, a conversion to Mn_2O_3 was observed (a). TGA for **compound 1** (b).

S5



Figure S2 DSC for **compound 1**.



Figure S3 TGA for **compound 2**.



Figure S4 DSC for **compound 2**.



Figure S5 CHN analyses for **compounds 1** (left) and **2** (right).



Figure S6 SEM images of **compound 1** as dispersed particles in water with different magnifications.





Figure S7 SEM images of **compound 1** as dried particles with different magnifications.



Figure S8 SEM images of **compound 2** as dried particles with different magnifications.



Figure S9 SEM-EDX mapping images of **compound 1** as dried particles.



Figure S10 SEM-EDX mapping images of **compound 2** as dried particles.



Figure S11 (HR)TEM images of **compound 1** as dried particles with different magnifications.



Figure S12 (HR)TEM images of **compound 2** as dried particles with different magnifications.



Figure S13 BET analysis for **compound 1**.



Figure S14 BET analysis for compound 2.



Figure S15 XPS spectra for **compounds 1** (a,b) and **2** (c,d).



Figure S16 XPS spectra for Mn 2p, Mn 3s, C 1s, and N 1s for compounds 2 (a-d).