Supporting Information

Synthesis and characterization of a series of novel

polyoxometalate-supported carbonyl manganese derivatives

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reference electrode is SCE.



Section 1: Summary of Keggin-type PMCDs reported in recent years

Fig. S1. Illustrations of some representative Keggin-type PMCDs reported in recent years

At the present time, the reported POM-supported metal carbonyl derivatives (PMCDs) are mainly concentrated on Lindqvist-type polyoxoanions, the reports on lacunary Keggin-type PMCDs are relatively rare, we summarize the Keggin-type PMCDs reported in the last few years. They can be classified as two categories on the degree of polymerization (Fig. S1). The number of dimer-PMCDs is slightly fewer than the monomer's. The common feature of all of them in structure is that $\{M(CO)_3\}$ (M=Mn/Re) fragments were embeded into or supported on the lacunary site of POM. The $[M(CO)_3]^+$ pendant is bonded to μ -O atoms from the POM units and achieves the 18-electron configuration. In order to make the PMCDs polymerization, appropriate linkers are needed. So, in this article, we introduce the transition metal in the reaction, synthesizing successfully a series of novel heterpolytungstates-based carbonyl manganese derivatives $[M_4(H_2O)_{10}(XW_9O_{33})_2\{Mn(CO)_3\}_2]^{n-}$ (X = Sb, Bi, and M = Mn, Mn_{3.5}W_{0.5}).

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Section 2: IR spectra of 1, 2, 3, 4 and Mn(CO)₅Br



Fig. S2. IR spectra (KBr pellets) of 1, 2, 3, 4 and Mn(CO)₅Br

Section 3: XRPD patterns of compounds 1, 2, 3 and 4



Fig.S3. Comparison of the simulated and experimental XRPD patterns: 1, 2, 3 and 4.

Section 4: The UV-vis spectra of 1, 2, 3 and 4

The UV-vis spectra of 1, 2, 3 and 4 were recorded in the mixed solvent solvent CH₃CN-H₂O (1/4, v/v). All display two absorption bands centered at ca. 270 and 350-400 nm (Fig. S4). The absorption bands in 270 nm can be assigned to the charge transfer transitions of the Ot \rightarrow W p π -d π charge-transfer transitions, suggesting the present of polyoxoanions, whereas the absorption band in 350-450 nm can be assigned to the charge transfer transition of Mn (d π) \rightarrow CO (π *), which is not obvious resulting from the lower concentration, indicating the existence of metal carbonyl units. In addition, the results of in situ UV-vis of 1, 2, 3 and 4 indicate that they were stable in aqueous solution.



Fig.S4 (a) The aging of the solution of 1 detected by in the in-situ UV-vis spectra; (b) The aging of the solution of 2 detected by in the in-situ UV-vis spectra; (c) The aging of the solution of 3 detected by in the in-situ UV-vis spectra; (d) The aging of the solution of 4 detected by in the in-situ UV-vis spectra.

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Section 5: Cyclic voltammograms of material, compounds 1 and 2 and the electrocatalytic properties of compounds 1 and 2 for the reduction of NO_2^-



Fig.S5 (a) Cyclic voltammograms of the comparation of the material with **1** at the scan rates of 100 mV s⁻¹ (b) Cyclic voltammograms of the comparation of the material with **2** at the scan rates of 100 mV s⁻¹. (c) Cyclic voltammograms of **1** with different concentrations of NaNO₂: 0, 0.5, 1.0 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 mM, respectively (from top to bottom) at a scan rate of 100 mV s⁻¹.(d) Cyclic voltammograms of **2** with different concentrations of NaNO₂: 0, 0.5, 1.0 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 mM, respectively (from top to bottom) at a scan rate of 100 mV s⁻¹.(d) Cyclic voltammograms of **2** with different concentrations of NaNO₂: 0, 0.5, 1.0 1.5, 2.0, 2.5, 3.0, 3.5, 4.0, 4.5, and 5.0 mM, respectively (from top to bottom) at a scan rate of 100 mV s⁻¹. The modified carbon paste electrode (CPE) was used as a working electrode and the reference electrode is SCE.