Supporting Information

Incorporation of Polyoxotungstate Complexes in Silica Spheres and In Situ Formation of Tungsten Trioxide Nanoparticles

Yuanyuan Zhao,[†] *Haimei Fan,*[‡] *Wen Li,*[†] *Lihua Bi,*[†] *Dejun Wang,*[‡] *and Lixin Wu**[†]

[†]State Key Laboratory of Supramolecular Structure and Materials, Jilin University, Changchun 130012, P. R. China; [‡]Alan G. MacDiarmid Institute College of Chemistry, Jilin University, Changchun 130012, P. R. China

To whom correspondence should be addressed. E-mail: wulx@jlu.edu.cn

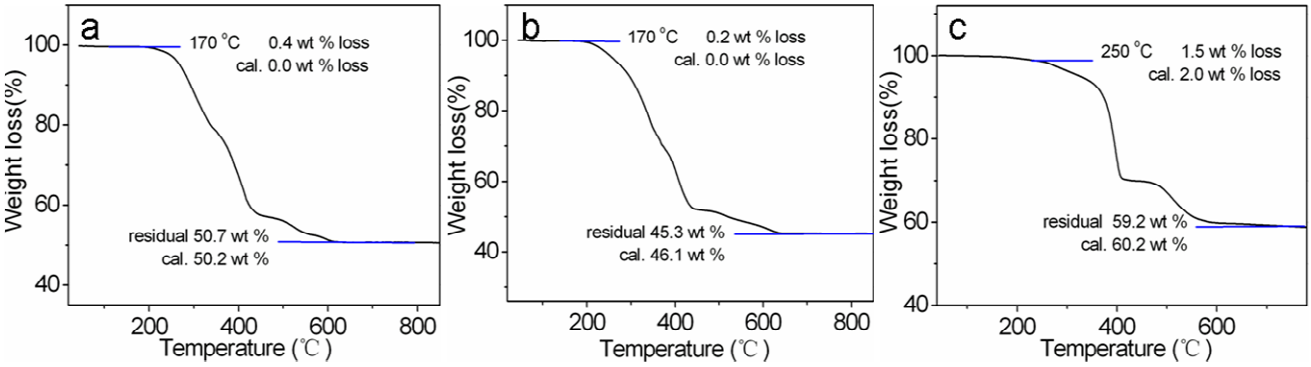

Figure S1. TGA spectra of (a) SEP-2, (b) SEP-3 and (c) SEP-4.

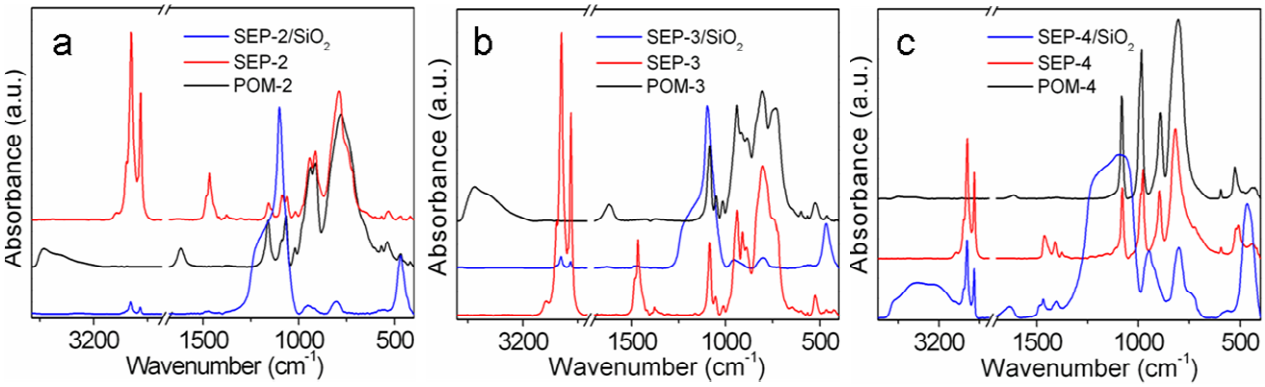

Figure S2. IR spectra of (a) POM-2 , SEP-2, and SEP-2/SiO_2; (b) POM-3 , SEP-3, and SEP-3/SiO_2; and (c) POM-4 , SEP-4, and SEP-4/SiO_2 in KBr.

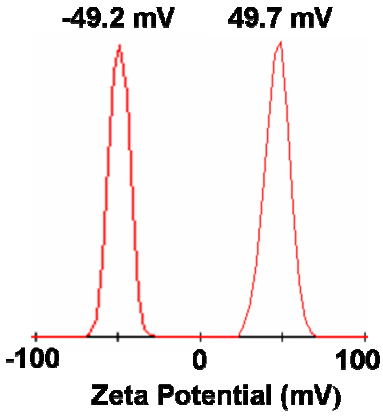

Figure S3. ζ potentials of S-1 (left) and CTAB/SEP-1 aggregates (right) in water.

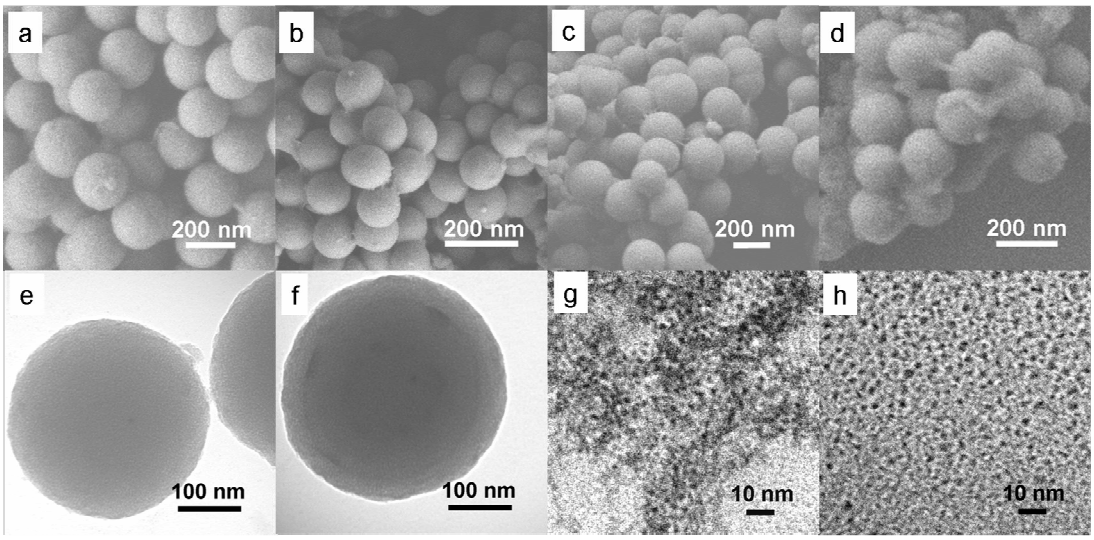

Figure S4. TEM images of (a) W-2, (b) W-3, (c) W-4, (d) W-5, (e) W-SEP-2/SiO_2, (f) W-SEP-3/SiO_2, (g) WO_3 from W-SEP-3/SiO_2; and (h) WO_3 from W-SEP-4/SiO_2.

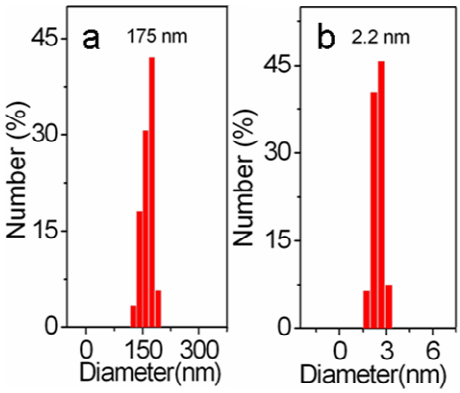

Figure S5. Distribution of particle size of (a) S-1 and (b) WO_3, counted from the statistic of Figure 3a and 3g, respectively.

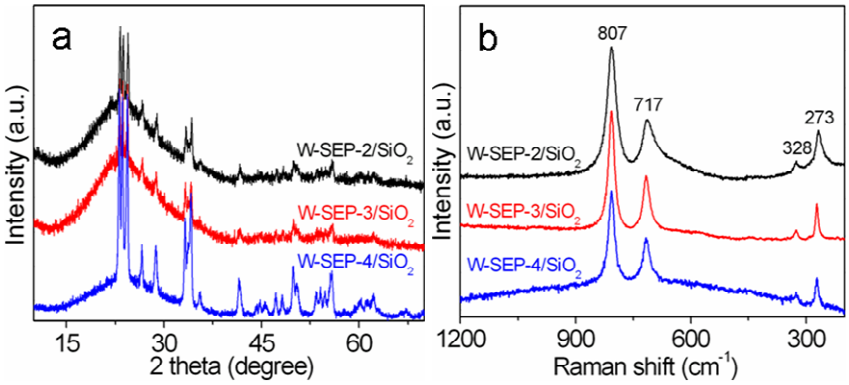

Figure S6. (a) XRD patterns and (b) Raman spectra of W-SEP-2/SiO_2, W-SEP-3/SiO_2 and

W-SEP-4/SiO_2.

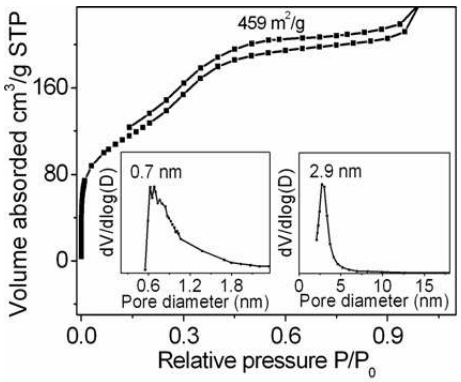

Figure S7. N_2 absorption curves, BET surface area and pore distribution of W'-2.

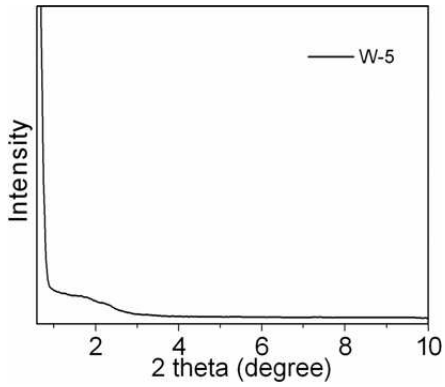

Figure S8. XRD pattern of W-5 in the low angle region.

Table S1 Summary of EA and TGA for Chemical Composition of Synthesized Complexes.

Name	**SEP-1**	**SEP -2**	**SEP -3**	**SEP -4**
Anticipated Chemical Formula	$(C_{38}H_{80}N)_9EuW_{10}O_{36}\cdot 9H_2O$	$(C_{38}H_{80}N)_{12}EuP_5W_{30}O_{110}$	$(C_{38}H_{80}N)_{14}NaP_5W_{30}O_{110}$	$(C_{38}H_{80}N)_3PW_{12}O_{40}\cdot 5H_2O$
Molecular Weight	7687.9	14194.5	15167.7	4620.3
Calculated Water Content (wt.%)	2.1	0.0	0.0	2.0
TGA, Found Water Loss (wt.%)	1.6	0.4	0.2	1.5
Anticipated Inorganic Residual	Eu_2O_3 WO_3	Eu_2O_3 WO_3	Na_2O WO_3	WO_3
Anticipated Residual Formula	$EuW_{10}O_{31.5}$	$EuW_{30}O_{91.5}$	$NaW_{10}O_{90.5}$	$W_{12}O_{36}$
Calculated Residual (wt.%)	32.5	50.2	46.1	60.2
TGA, Found Residual (wt.%)	32.4 (840 ^{o}C)	50.7 (>600 ^{o}C)	45.4 (>600 ^{o}C)	59.7 (>600 ^{o}C)
EA, Calculated (wt.%)	C 53.43; H 9.68; N 1.64	C 38.58; H 6.82; N 1.18	C 42.13; H 7.44; N 1.29	C 29.64; H 5.45; N 0.91
EA, Found (wt.%)	C 52.98; H 9.76; N 1.63	C 38.98; H 6.47; N 0.96	C 42.66; H 7.03; N 0.93	C 29.35; H 5.07; N 0.66
Venue	Figure 1	Figure S1a	Figure S1b	Figure S1c

Table S2. Summary of IR vibration assignments of POMs, SEPs and SEP/SiO2 hybrid spheres.

POM-1 (cm^{-1})	POM-2 (cm^{-1})	POM-3 (cm^{-1})	POM-4(cm^{-1})	Vibration Assignments
--	1161,1089,1061, 1021	1085,1051,1016	1082	v (P-O_a)
945	983,939	940	984	v_{as} (W-Od)
895	914	914,885	891	v_{as} (W-O_b-W)
843,778,703	779	806,736	803	v_{as} (W-O_c-W)
SEP-1 (cm^{-1})	**SEP-2 (cm^{-1})**	**SEP-3 (cm^{-1})**	**SEP-4 (cm^{-1})**	**Vibration Assignments**
3427	--	--	--	v (O–H) of H_2O
2956	2956	2956	2955	v_{as} (C–H) of CH_3
2920	2921	2920	2920	v_{as} (C–H) of CH_2
2850	2851	2851	2851	v_s (C–H) of CH_2
1630	--	--	--	δ (O-H) of H_2O
1487	1485	1485	--	δ (C–H) of CH_2N
1468	1468	1468	1463	δ (C–H) of CH_2
1379	1378	1379	1377	δ (C–H) of CH_3
--	1062,1018	1055,1086,1012	1080	v (P-O_a)
941	942	939	978	v_{as} (W-Od)
924	915	893, 910	895	v_{as} (W-O_b-W)
839,802,774	789	803,780,741	818	v_{as} (W-O_c-W)
SEP-1/SiO_2 (S-5)(cm^{-1})	**SEP-2/SiO_2 (cm^{-1})**	**SEP-3/SiO_2 (cm^{-1})**	**SEP-4/SiO_2 (cm^{-1})**	**Vibration Assignments**
3297	--	--	3402	v (O-H) of H_2O
2958	2956	2956	2956	v_{as} (C–H) of CH_3
2920	2924	2924	2922	v_{as} (C–H) of CH_2
2850	2854	2853	2852	v_s (C–H) of CH_2
1487	--	--	--	δ (C–H) of CH_2N
1468	1469	1468	1468	δ (C–H) of CH_2
1082	1101	1097	1088	combination of v (P-O_a), v_{as}(Si-O-Si)
867,890,939,960	953,938,918,900	955,937,918,900	947,918	combination of v(Si-O-H), v_{as}(W-Od), v_{as}(W-O_b-W)
777,796,818	804, --, --	800, --, --	800,742,721	combination of v_s(Si-O-Si), v_{as}(W-O_c-W)

Table S3. EA data of SEP-1/SiO_2 (S-2), SEP-2/SiO_2, SEP-3/SiO_2 and corresponding W-SEP-1/SiO_2 (W-2), W-SEP-2/SiO_2, W-SEP-3/SiO_2.

	C (%)	H (%)	N (%)
S-2	8.90	2.35	0.55
W-2	--	0.40	--
S-SEP-2/SiO_2	12.56	2.91	0.45
W-SEP-2/SiO_2	0.39	0.33	--
S-SEP-3/SiO_2	11.69	2.85	0.54
W-SEP-3/SiO_2	0.33	0.42	--

Table S4. BET surface area and pore distribution of W-SEP-1/SiO_2.

	BET m^2/g	Mesopore width (nm)	Micropore width (nm)
S-1	16.8	--	--
S-2	12.5	--	--
S-3	16.0	--	--
S-4	8.0	--	--
S-5	4.6	--	--
W-0	85	--	0.8
W-1	184	2.0	--
W-2	205	2.5	--
W-3	326	2.1	--
W-5	395	2.2	--
W'-2	459	2.9	0.7
W-SEP-2/SiO_2	410	2.4	0.8
W-SEP-3/SiO_2	527	1.8	0.7