Supporting Information

Necessarity of calcination in preparation of phosphotungstic acid@TiO_2 composites? A case study on facile sol-gel synthesis of nanospheres and their superior performance in catalytic oxi-desulfurization

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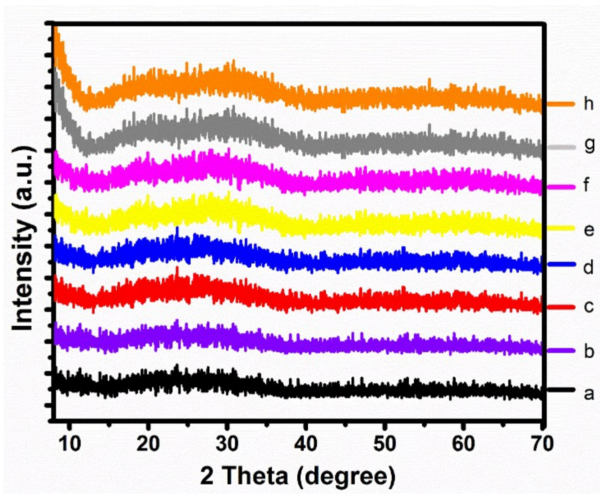


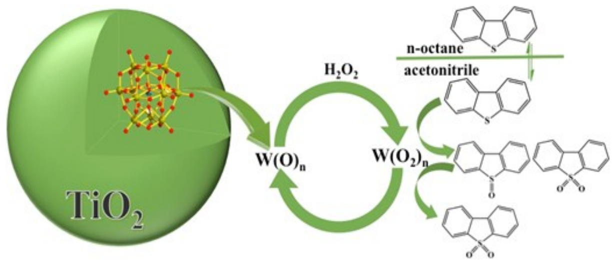
Fig. S1. Powder XRD patterns of PW_{12}@TiO_2 spherical samples: a. uncal-10_ PW_{12}@TiO_2, b. cal-10_ PW_{12}@TiO_2, c. uncal-20_ PW_{12}@TiO_2, d. cal-20_ PW_{12}@TiO_2, e. uncal-30_ PW_{12}@TiO_2, f. cal-30_ PW_{12}@TiO_2, g. uncal-40_ PW_{12}@TiO_2, and h. cal-40_ PW_{12}@TiO_2.

Table S1. ICP element analysis results of spherical un-calcinated PW_{12}@TiO_2 with different PW_{12} loading amounts

Samples	μg/mL				PW_{12} content	
	P	W	Ti	W/P	Gel[a] (wt%)	Product[b] (wt%)
Un-cal_PW_{12}@TiO_2 (10 wt%)	1.15	76.5	546	11.7	10	9.5
Un-cal_PW_{12}@TiO_2 (20 wt%)	2.25	214	388	11.6	20	19.6
Un-cal_PW_{12}@TiO_2 (30 wt%)	3.02	260	272	11.8	30	29.3
Un-cal_PW_{12}@TiO_2 (40 wt%)	4.14	321	155	11.7	40	39.4

[a] theoretical loading amount of PW_{12} calculated from the ratio of the raw materials during the sample preparation process; [b] actual loading amount of PW_{12} calculated from the results of ICP analysis.

The PW_{12} contents in final un-calcinated products of $PW_{12}@TiO_2$ catalysts are detected by ICP and are listed in Table S1. The determined loadings of PW_{12} are found very close to the expected values, indicating minimum loss of PW_{12} in our prepared process.



Scheme S1 The schematic diagram illustrating reaction mechanism of ECODS in this work.

(i) In the presence of excess amount of H_2O_2, metal precursor of phosphotungstic acid ($W(O)_n$) is peroxidized and disaggregated to form anionic peroxometal complex ($W(O_2)_n$) and as discussed in the main manuscript the DBT concentration in n-octane phase reached an equilibrium value of 47% in n-octane and 53% in acetonitrile before the addition of catalyst at room temperature, due to liquid–liquid extraction processes.

$$W(O)_n^{-}Q^{+} \xrightleftharpoons{k'_1/k'_2} W(O)_n^{-} + Q^{+} \tag{1}$$

$$W(O)_n^{-} + H_2O_2 \xrightarrow{k_2} W(O_2)_n^{-} + H_2O \tag{2}$$

$$W(O_2)_n^{-} + Q^{+} \xrightleftharpoons{k'_3/k'_4} W(O_2)_n^{-}Q^{+} \tag{3}$$

(ii) DBT is oxidized by the peroxometal complex in the acetonitrile phase rapidly into more polar products, such as sulfoxides and sulfones and these species reside in the polar phase, acetonitrile.

$$W(O_2)_n^{-}Q^{+} + DBT \xrightarrow{k_1} Sulfoxide + W(O)_n^{-}Q^{+} \tag{4}$$

$$Sulfoxide + W(O_2)_n^{-}Q^{+} \xrightarrow{k_3} Sulfones + W(O)_n^{-}Q^{+} \tag{5}$$

(iii) The generated reduced species are responsible for continuing the next catalytic cycle. [s1-s7]

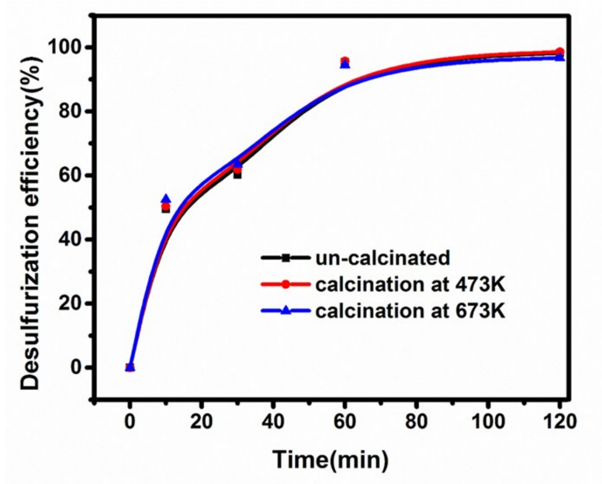


Fig. S2. Desulfurization efficiencies of 30_PW_{12}@TiO_2 nano spheres prepared at different calcination temperatures. Reaction condition: O/S, 10; catalyst amount, 0.5% of n-octane; temperature, 60 ^oC; reaction time, 2h.

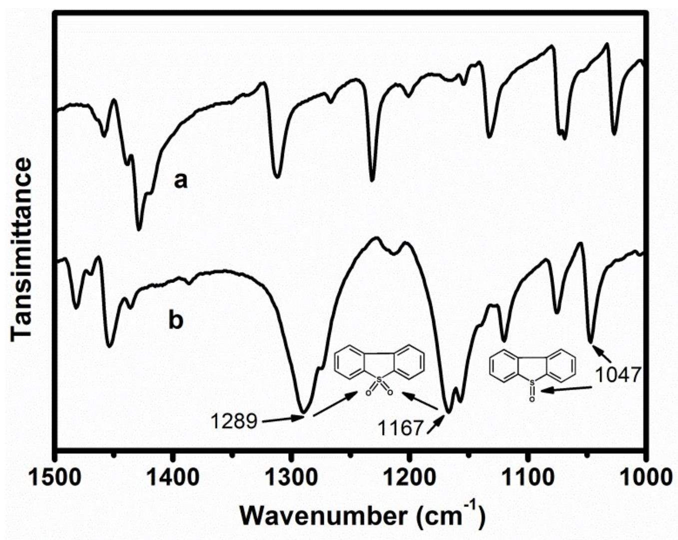


Fig. S3. IR spectra of DBT (a) and its oxidation products (b)

In order to estimate the quantity of PW_{12} that has lost during the catalytic activity after 10th use of ECODS, the recycled un-calcinated 30_PW_{12}@TiO_2 was subjected to ICP elemental analysis to estimate the quantities of PW_{12} content and shown as in table below.

Table S2. ICP element analysis results of spherical fresh and 10th used un-calcinated 30_PW_{12}@TiO_2

Samples	μg/mL				PW_{12} content	
	P	W	Ti	W/P	Gel[a] (wt%)	Product[b] (wt%)
Un-cal_PW_{12}@TiO_2 (Fresh 30 wt%)	3.02	260	272	11.8	30	29.3
Un-cal_PW_{12}@TiO_2 (10^{th} used 30 wt%)	2.95	254	270	11.7	-	28.6

[a] theoretical loading amount of PW_{12} calculated from the ratio of the raw materials during the sample preparation process; [b] actual loading amount of PW_{12} calculated from the results of ICP analysis.

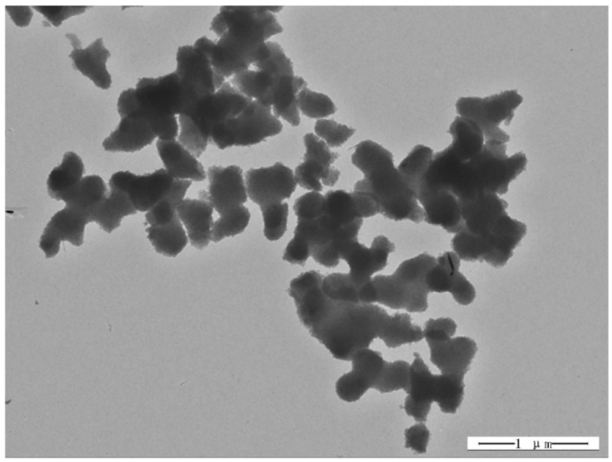


Fig. S4. TEM image of uncal-30_PW_{12}@TiO_2 after 10th catalytic cycle.

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