Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Polyoxometalates encapsulated into hollow double-shelled nanospheres as amphiphilic nanoreactors for effective oxidative desulfurization

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Table S1. Surface area and porosity data of PMo_{12}/$AmHMSiO_2$@C, $AmHMSiO_2$@C and $HMSiO_2$@C.

Materials	Surface area (m^2/g)	Pore volume (cm^3/g)	Average pore Diameter (Å)
PMo_{12}/$AmHMSiO_2$@C	57	0.54	0.8
$AmHMSiO_2$@C	229	0.77	2.4
$HMSiO_2$@C	740	1.57	2.5

Table S2. The elemental analysis of PMo_{12}/$AmHMSiO_2$@C nanoreactor.

Sample	Mo	P	C	H	N
PMo_{12}/$AmHMSiO_2$@C（wt%）	14.19	5.91	17.89	2.38	1.62

Table S3. Comparison of heterogeneous catalysts for oxidation of DBT.

Catalyst	H_2O_2/DBT mol/mol	Temp. (°C)	Time (h)	Conv. (%)	Ref.
PMo_{12}/AmHMSi@C	3	40	3	>99	This work
SiO_2@C-dots/PW_{12}[a]	3	50	3	100	1
Ti(IV)/SiO_2	5	60	8	>99	2
Zr(IV)/PMMA[b]	3.5	65	24	84	3
$[Cu(dpa)(acac)]_2[V_6O_{11}(OMe)_8]$[c]	4	40	6	100	4
PW_{11}Zn-MOF[d]	50	50	6	100	5
PMo_{12}/BzPN-SiO_2[e]	3	60	3	100	6

[a] SiO_2@C-dots loading calcined PW_{12} in octane-acetonitrile system.

[b] Zr oxoclusters reinforced poly(methylmethacrylate) (PMMA) in octane-acetonitrile system.

[c] Alkoxohexavanadate-based Cu-complex in decalin-acetonitrile biphasic system.

[d] PW_{11}Zn@MOF in octane-[BIMIM] PF_6 system.

[e] PMo_{12} immobilized on phosphazene-functionalized silica in octane-H_2O system.

The conversion of DBT, H_2O_2/DBT molar ratio, reaction temperature and reaction time from recent investigations were summarized in (Table S3). For example, a core-shell catalyst, SiO_2@C-dots/PW_{12}, synthesized by loading PW_{12} and carbon dots on a solid silica core, can convert 100% of DBT in 3 h at 50 °C, but after three recycles its catalytic activity decreased to 80.4%. 99% of DBT was oxidized by titanium grafted on silica at 60 °C with H_2O_2/DBT molar ratio of 5, but a long reaction time (8 h) was needed. For Zr(IV)/poly(methlymethacrylate) (PMMA), after 24 h only a conversion of 84% was obtained at 65°C. Recently, an alkoxohexavanadate-based catalyst was synthesized in our group and at 40 °C DBT can be completely removed in 6 h. The PW_{11}Zn@MOF composite gave 100% conversion of DBT at 50 °C in 6 h, but a large amount of excess H_2O_2 was used. The PMo_{12}/BzPN-SiO_2 can convert 100% DBT in 3 h, but the oxidative desulfurization was performed at 60℃. In comparison, our PMo_{12}/AmHMSiO_2@C nanoreactor converts >99% of DBT in 3 h with H_2O_2/DBT molar ratio of 3 and the temperature (40 °C) in our catalytic reaction is lower than that in most other reports. Importantly, both catalytic activity and structure of the nanoreactor are maintained after five constant cycles.

Fig. S1. (a) SEM image of $HMSiO_2$@C. (b) TEM image of $HMSiO_2$@C. (c) The digital image of SiO_2@RF. (d) The digital image of $HMSiO_2$@C.

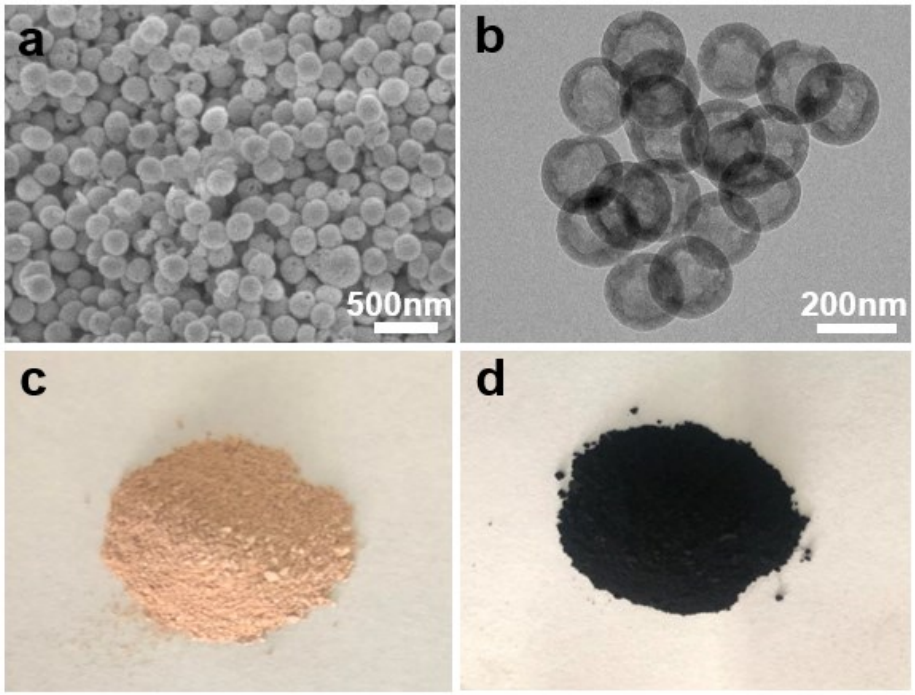


Fig. S2. (a) SEM image of AmHMSiO_2@C. (b) TEM image of AmHMSiO_2@C. (c) SEM image of PMo_{12}/AmHMSi@C. (d) TEM image of PMo_{12}/AmHMSi@C.

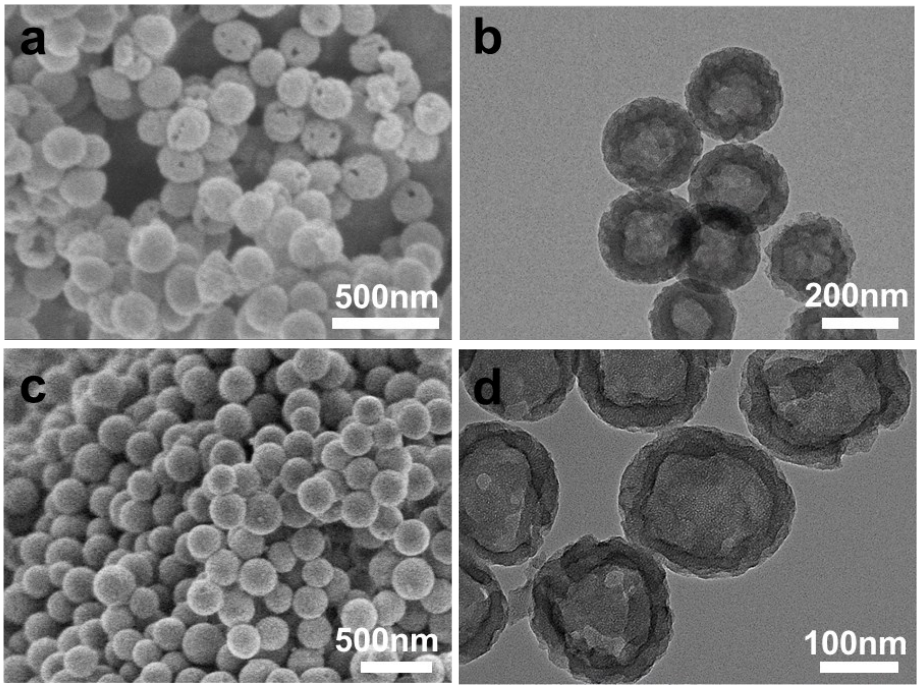


Fig.S3. The IR spectra of SiO_2@C and Modify-SiO_2@C

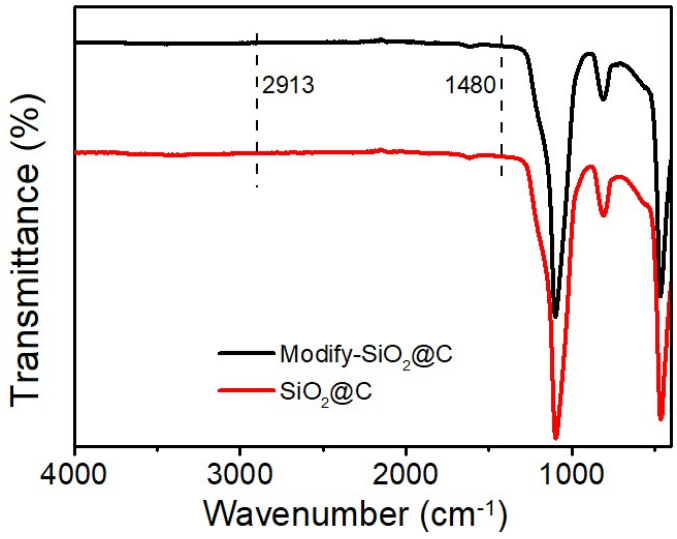
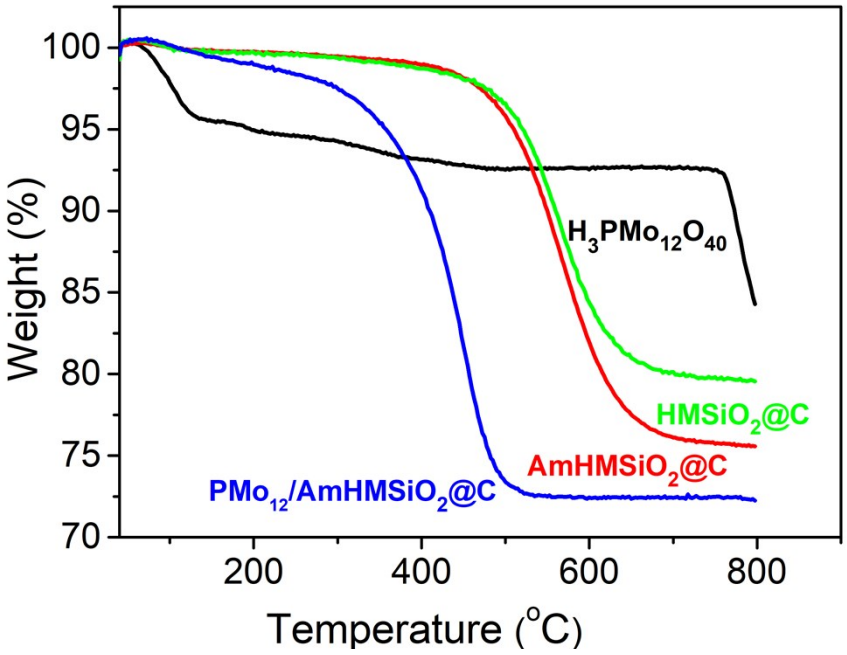


Fig. S4 TG curves of $HMSiO_2$@C,$AmHMSiO_2$@C, PMo_{12}/$AmHMSiO_2$@C and $H_3PMo_{12}O_{40}$.



According to the ICP and element analysis results, the loading amount of PMo_{12} is about 20.1% and as a result the $AmHMSiO_2$@C support accounts for 79.9% in PMo_{12}/$AmHMSiO_2$@C. According to the TG curves of $AmHMSiO_2$@C support, the ratio of organosilanes and amorphous carbon to the SiO_2 is 1:2.9. Therefore, the weight percentage of SiO_2 = 79.9%*(2.9/3.9) = 59.4%. The ratio of SiO_2 to amorphous carbon is 3.7:1, which is determined according to the TG curve of $HMSiO_2$@C. Therefore, the weight percentage of amorphous carbon = 59.4%/3.7 = 16.0%. As a result, the weight percentage of organosilanes = 79.9% - 59.4% - 16.0% = 4.5%.

Fig. S5. (a) TEM image of $PMo_{12}/AmSSiO_2$. (b) The IR spectra of PMo_{12} and $PMo_{12}/AmSSiO_2$.

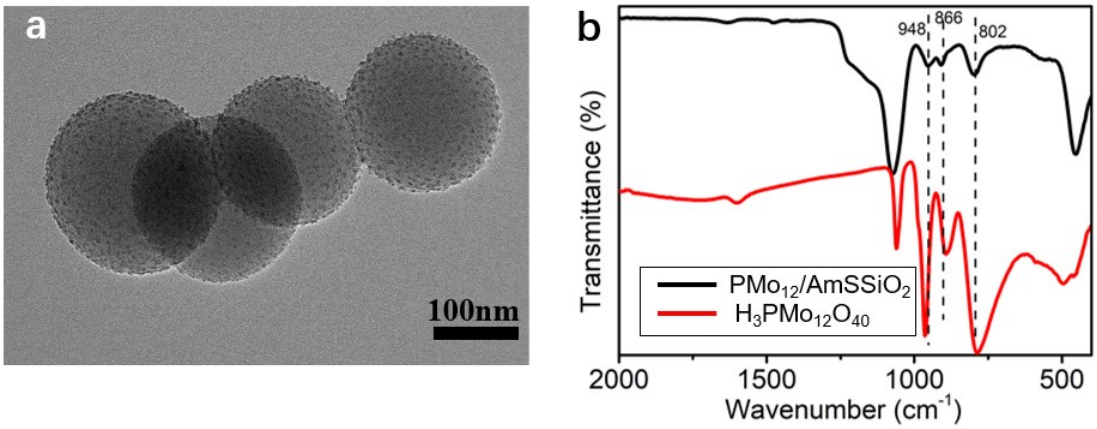


Fig. S6. (a) TEM image of $PMo_{12}/AmSMSiO_2@C$ (b) The IR spectra of $PMo_{12}/AmSMSiO_2@C$ and PMo_{12}.

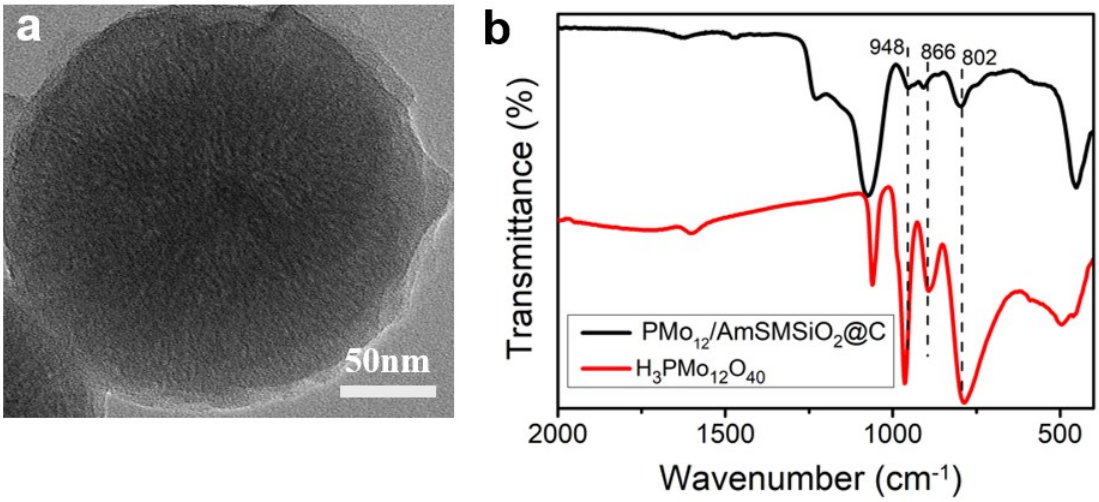


Fig. S7. (a) TEM image of $PMo_{12}/HMSiO_2$@C. (b) The IR spectra of $PMo_{12}/HMSiO_2$@C and PMo_{12}.

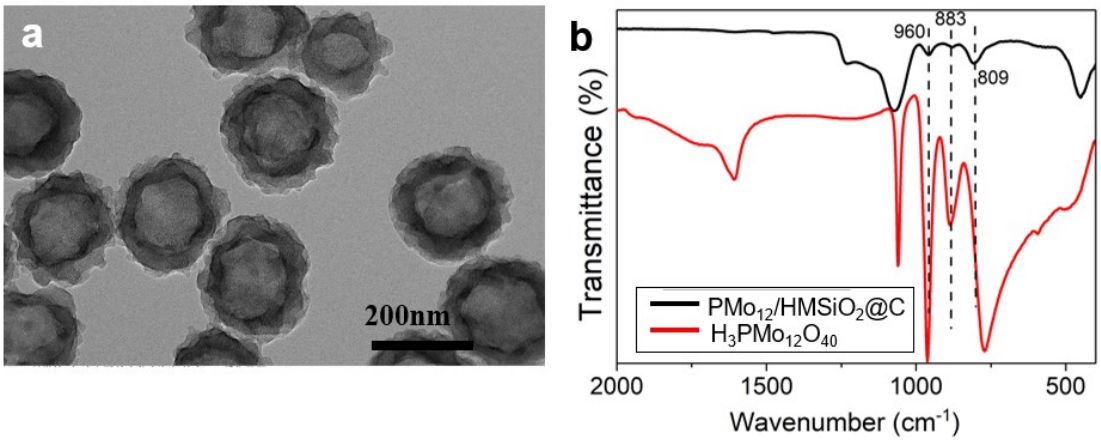


Fig. S8. XPS spectrum of $PMo_{12}/AmHMSiO_2$@C nanoreactor.

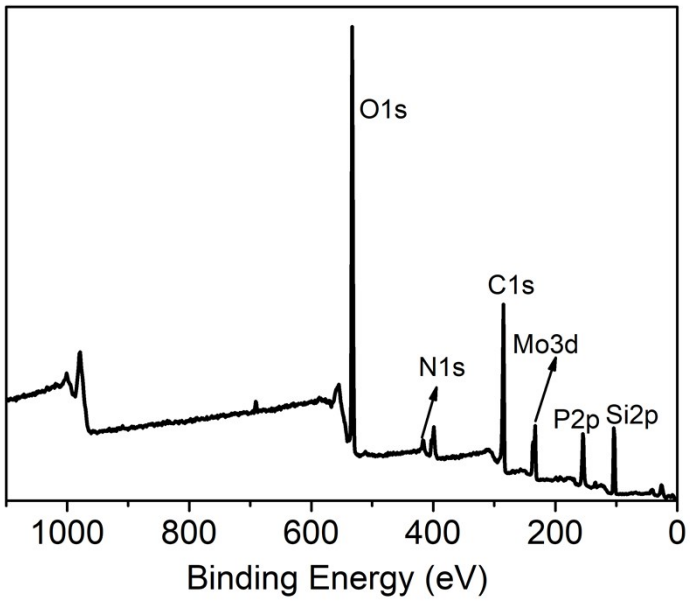
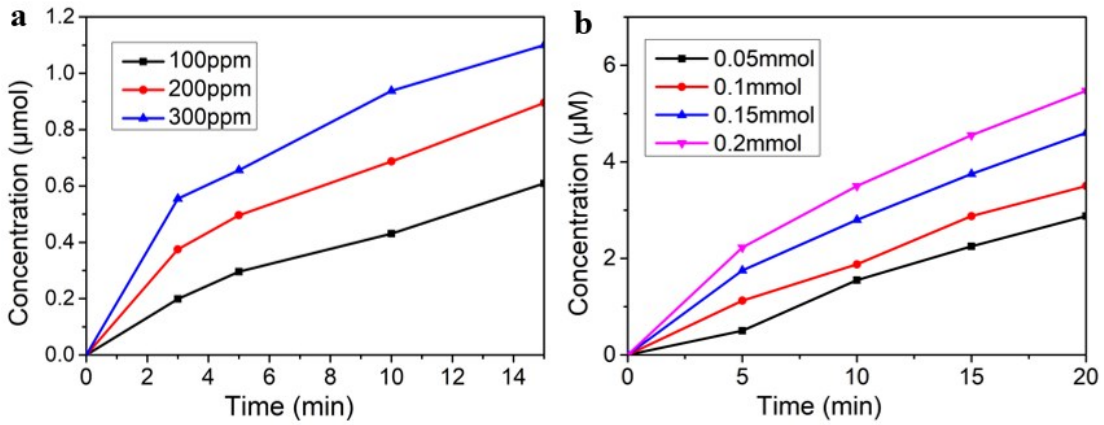


Fig. S9. (a) Concentration-time-course plot for DBT oxidation with different concentration of DBT. Reaction conditions: $PMo_{12}/AmHMSiO_2$@C (0.002 mmol), 30% H_2O_2 (0.15 mmol), n-octane (2 mL) containing DBT (100, 200, or 300 ppm), acetonitrile (2 mL) at 40 °C for 15 min. (b) Concentration-time-course plot for DBT oxidation with different amount of H_2O_2. Reaction conditions: $PMo_{12}/AmHMSiO_2$@C (0.002 mmol), 30% H_2O_2 (0.05, 0.10, 0.15 or 0.20 mmol), n-octane (2 mL) containing DBT (800 ppm), acetonitrile (2 mL) at 40 °C for 20 min.



Notes and references

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