Supporting Information

Reduced Polyoxomolybdate Immobilized on Reduced Graphene Oxide for Rapid Catalytic Decontamination of Sulfur Mustard Simulant

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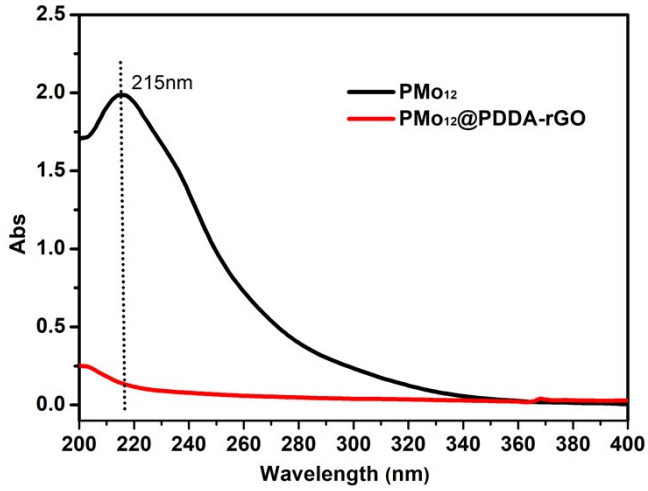

Figure S1. Liquid-phase UV-Vis spectrum from leaching test of PMo_{12}@PDDA-rGO immersed in water for 12 h.

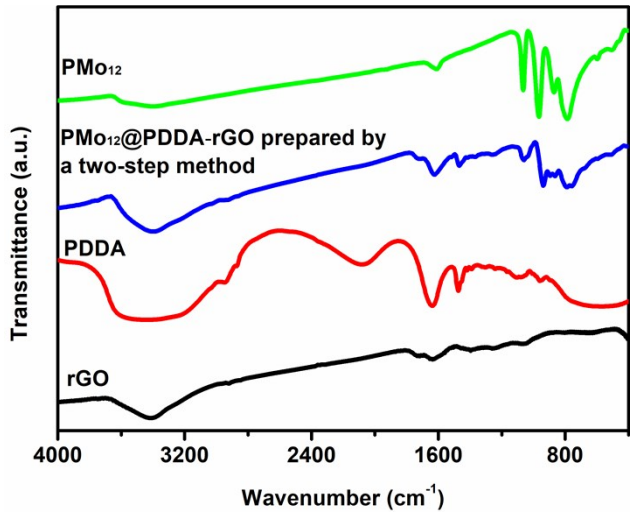

Figure S2. FT-IR spectra of PMo_{12}@PDDA-rGO prepared by a two-step method, rGO, PDDA and PMo_{12}.

PMo_{12}@PDDA-rGO prepared by a two-step method as follows. The mixture of PDDA (0.3 mL) and GO (2 mg/mL, 15 mL) was first treated under hydrothermal conditions (100 ºC) for 10 h, and then the resulting PDDA-rGO was dispersed in the aqueous solution of PMo_{12} (5 mmol/L, 10 mL). The reaction mixture was stirred for 5 h at room temperature, and the solid product was separated by centrifugation, and washed with deionized water for several times to remove any unloaded PMo_{12}. The obtained product was frozen in liquid nitrogen and dried in freeze dryer for two days.

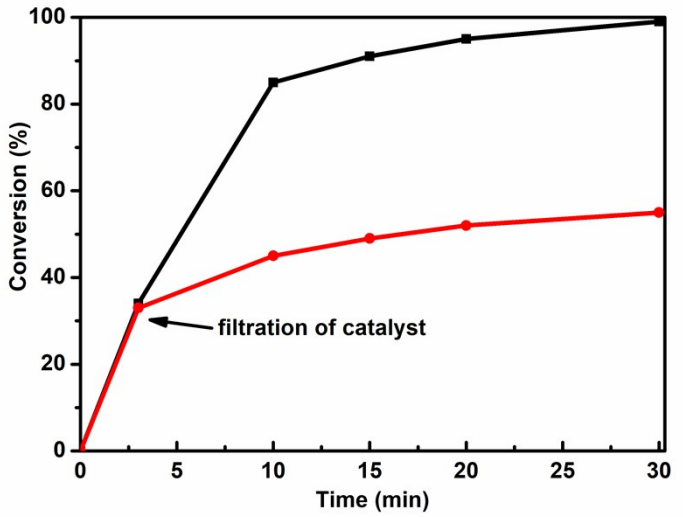

Figure S3. Leaching test for CEES degradation using PMo_{12}@PDDA-rGO prepared by a two-step method.

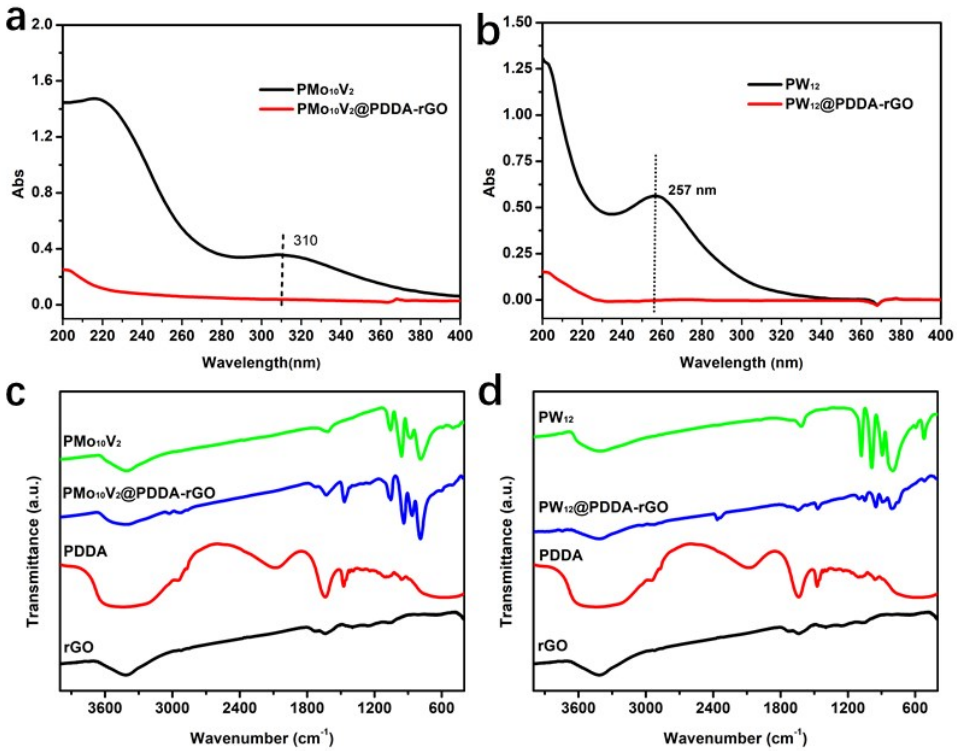

Figure S4. Liquid-phase UV-vis spectra from leaching test of (a) $PMo_{10}V_2$@PDDA-rGO and (b) PW_{12}@PDDA-rGO immersed in water for 12 h; FT-IR spectra of (c) $PMo_{10}V_2$@PDDA-rGO and (d) PW_{12}@PDDA-rGO.

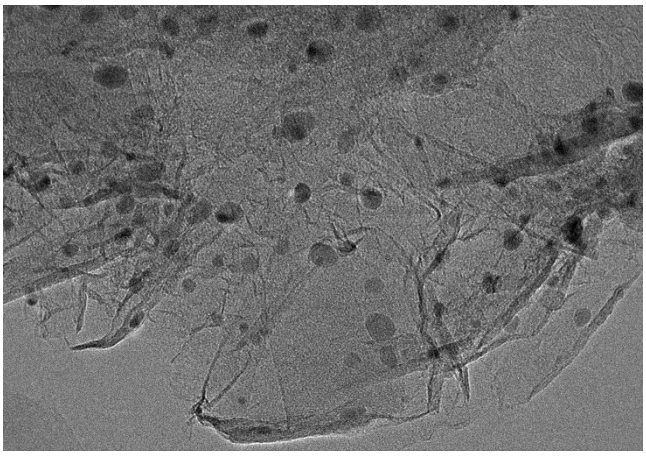

Figure S5. TEM image of PMo_{12}@PDDA-rGO

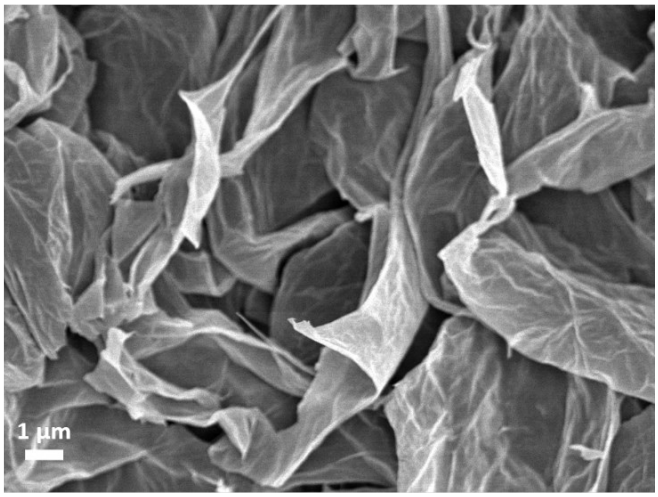

Figure S6. SEM image of rGO.

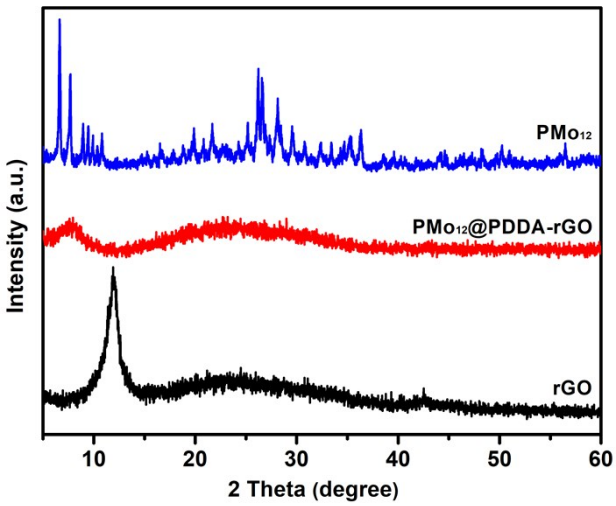

Figure S7. PXRD patterns of PMo_{12}@PDDA-rGO, PMo_{12} and rGO.

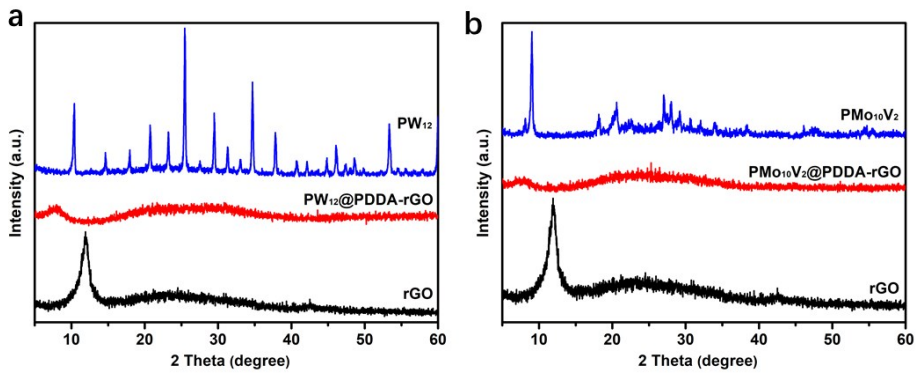

Figure S8. (a) PXRD patterns of PW_{12}@PDDA-rGO, rGO and PW_{12}; (b) PXRD patterns of $PMo_{10}V_2$@PDDA-rGO, rGO and $PMo_{10}V_2$.

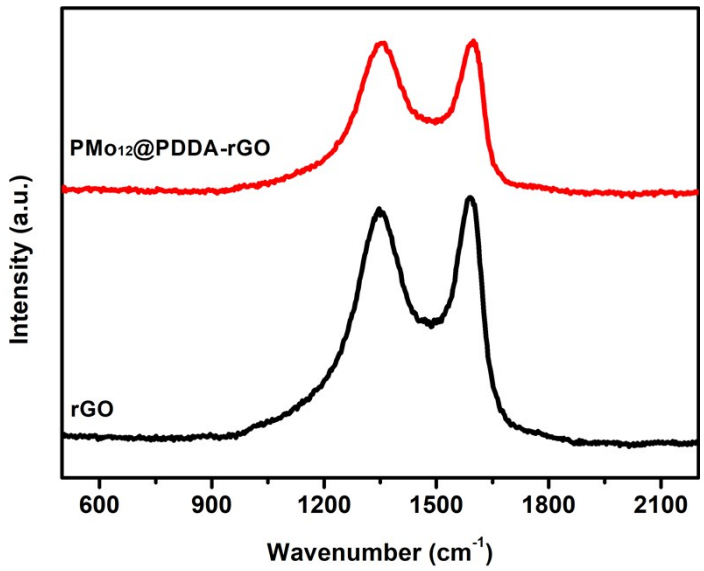

Figure S9. Raman spectra of PMo_{12}@PDDA-rGO and rGO.

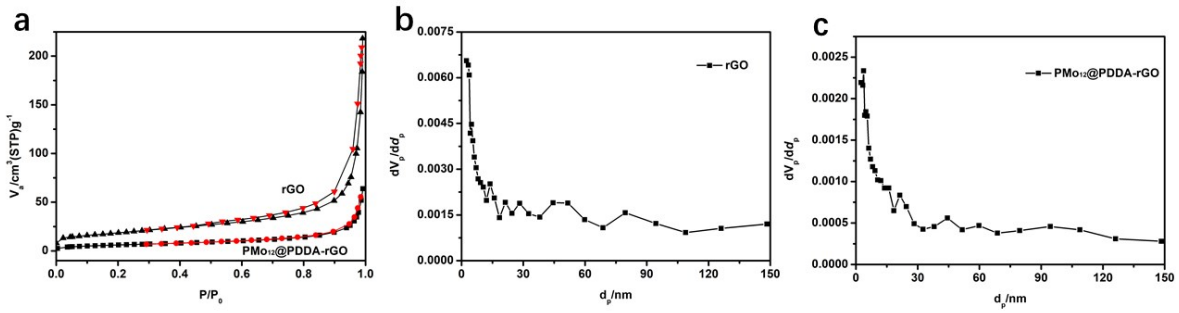

Figure S10. (a) The N_2 adsorption-desorption isotherms of PMo_{12}@PDDA-rGO and rGO; Pore size distributions of (b) rGO and (c) PMo_{12}@PDDA-rGO.

Sample	Contact angle
PMo_{12}	39° 
rGO	70° 
PMo_{12}@PDDA-rGO	61° 

Figure S11. Contact angle images of PMo_{12}@PDDA-rGO, PMo_{12} and rGO.

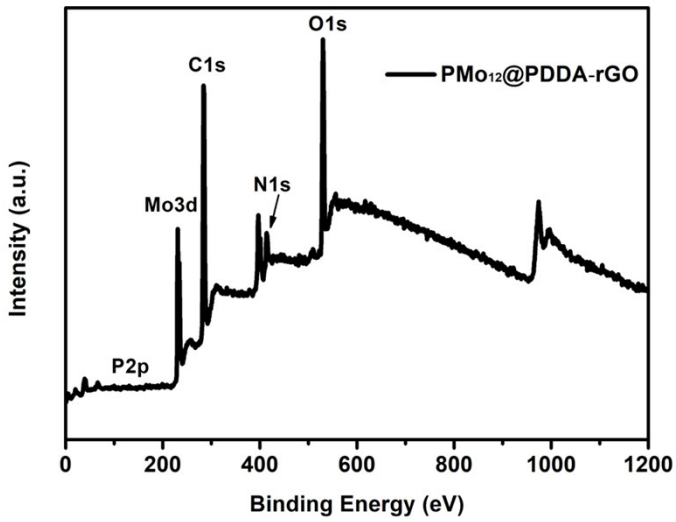

Figure S12. XPS survey spectra of PMo_{12}@PDDA-rGO.

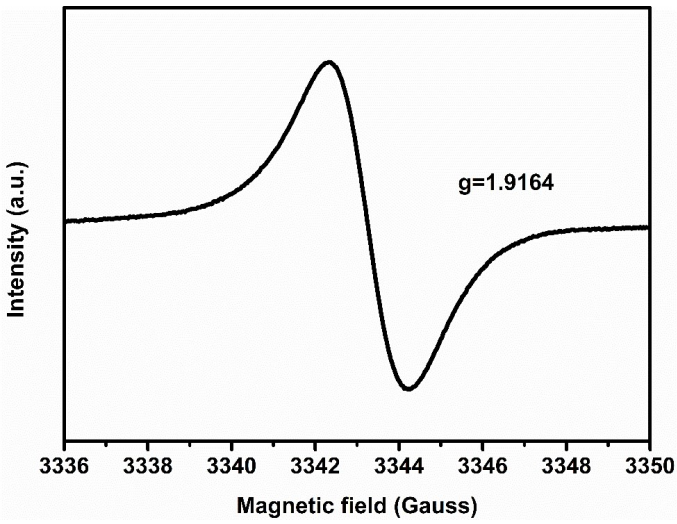

Figure S13. EPR spectrum of PMo_{12}@PDDA-rGO.

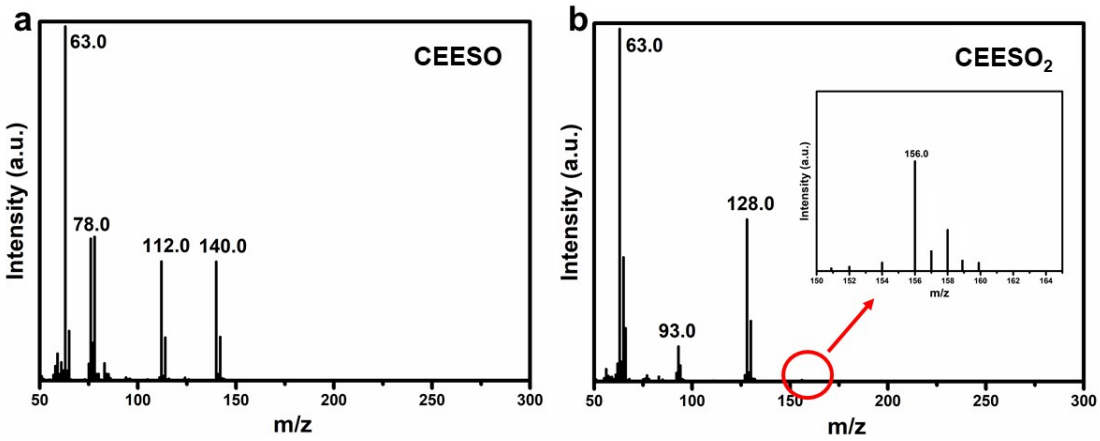

Figure S14. Mass spectrum of (a) CEESO and (b) $CEESO_2$.

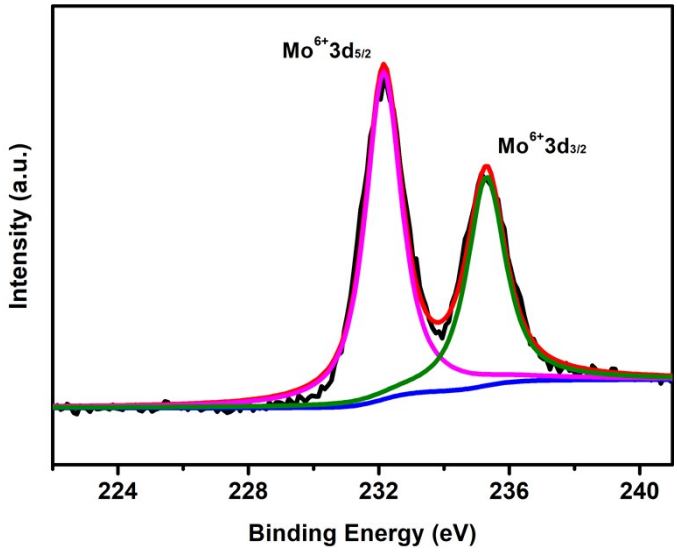

Figure S15. XPS spectra for the Mo3d core level spectrum of $PMo_{10}V_2$@PDDA-rGO.

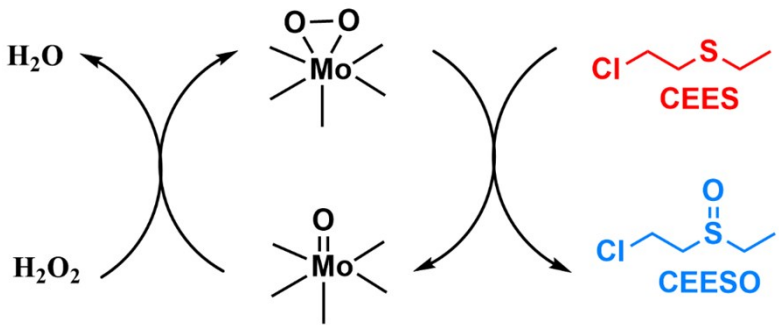

Figure S16. Possible reaction mechanism of CEES decontamination using PMo_{12}@PDDA-rGO as catalyst.

Table S1. The elemental analysis of PMo_{12}@PDDA-rGO.

Sample	Mo(wt%)	P(wt%)	PMo_{12}(wt%)
PMo_{12}@PDDA-rGO-26%	16.15	0.28	26
PMo_{12}@PDDA-rGO-33%	21.10	0.49	33
PMo_{12}@PDDA-rGO-45%	28.46	0.82	45
PMo_{12}@PDDA-rGO-47%	29.91	0.88	47

Table S2. Comparison of the heterogeneous catalysts for the oxidative degradation of sulfur mustard simulant.

Catalyst	Oxidant	Loading (mmol)	TON[e]	TOF (min^{-1})[f]	Conv. (%)	Sel. (%)[a]	Time (min)	ref.
PMo_{12}@PDDA-rGO	3% H_2O_2	0.005	49.5	1.7[g]	99	90	30	This work
Mg_3Al-LDH-Nb_6	3% H_2O_2	0.003	158.3	1.3[h]	95	97	120	1
Zn_2Cr-LDH-$PW_{11}Ni$	3% H_2O_2	0.0015	326.7	1.8[i]	98	94	180	2
Nb_2O_5	30% H_2O_2	0.075	3.7	0.012[j]	>99	73	300	3
Nb-SAP[b]	30% H_2O_2	0.0028	95.9	0.2[k]	>98	73	480	4
Fe-DECON1[c]	30% H_2O_2	0.043	1.3	0.0009[l]	20	-	1440	5
V-APMS[d]	TBHP	0.031	1.3	0.02[m]	97	75.6	60	6
PW_{12}@NU-1000	30% H_2O_2	0.0017	20.8	10.4[n]	98	57	20	7

[a] The selectivity for CEESO; [b] Nb-SAP: Niobium (V) Saponite Clay; [c] Fe-DECON1: Iron-montmorillonite clays; [d] V-APMS: vanadium-doped acid-prepared mesoporous silica; [e] TON = moles product / moles of total catalytic clusters; [f]TOF = moles product / (moles of total catalytic clusters × amount of time); [g] Time = 90 min; [h] Time = 120 min; [i] Time = 180 min; [j] Time = 300 min; [k] Time = 480 min; [l] Time = 1440 min; [m] Time = 60 min; [n] Time = 2 min.

As shown in Table S2, the TON or TOF of PMo_{12}@PDDA-rGO is not better than that of Mg_3Al-LDH-Nb_6 or Zn_2Cr-LDH-$PW_{11}Ni$ we reported previously. But for the detoxification of chemical warfare agents the decontamination efficiency is a key point to be concern. The decontamination rate of CEES catalyzed by PMo_{12}@PDDA-rGO is much better than that by Mg_3Al-LDH-Nb_6 or Zn_2Cr-LDH-$PW_{11}Ni$ as high POM loading can be achieved with the help of PDDA.

Table S3. The oxidative decontamination of CEES catalyzed by PMo_{12}@PDDA-rGO

in the presence of radical scavengers.

Radical scavengers	Time (min)	Conv. (%)	Sele. (%)
-	30	98	90
p-benzoquinone ($\cdot O_2^-/\cdot O_2H$)	30	97	88
tert-butyl alcohol ($\cdot OH$)	30	98	89
diphenylamine ($\cdot OH$)	30	98	90

Reaction conditions: PMo_{12}@PDDA-rGO (20 mg), CEES (0.25 mmol), 1,3-dichlorobenzene (0.125 mmol), 3 wt% aqueous H_2O_2 (internal standard, 0.275 mmol), radical scavengers (0.25 mmol) and acetonitrile (4 mL) at room temperature.

References

1 J. Dong, H. J. Lv, X. R. Sun, Y. Wang, Y. M. Ni, B. Zou, N. Zhang, A. X. Yin, Y. N Chi and C. W. Hu, *Chem.-Eur. J.*, 2018, **24**, 19208-19215.

2 X. R. Sun, J. Dong, Z. Li, H. F. Liu, X. T. Jing, Y. N. Chi and C. W. Hu, *Dalton Trans.*, 2019, **48**, 5285-5291.

3 C. Bisio, F. Carniato, C. Palumbo, S. L. Safronyuk, M. F. Starodub, A. M. Katsev, L. Marchese and M. Guidotti, *Catal. Today*, 2016, **277**, 192-199.

4 F. Carniato, C. Bisio, R. Psaro, L. Marchese and M. Guidotti, *Angew. Chem. Int. Ed.*, 2014, **53**, 10095-10098.

5 F. Carniato, C. Bisio, C. Evangelisti, R. Psaro, V. Dal Santo, D. Costenaro, L. Marchese and M. Guidotti, *Dalton Trans.*, 2018, **47**, 2939-2948.

6 C. R. Ringenbach, S. R. Livingston, D. Kumar and C. C. Landry, *Chem. Mater.*, 2005, **17**, 5580-5586.

7 C. T. Buru, P. Li, B. L. Mehdi, A. Dohnalkova, A. E. Platero-Prats, N. D. Browning, K. W. Chapman, J. T. Hupp and O. K. Farha, *Chem. Mater.*, 2017, **29**, 5174-5181.