Electronic Supplementary Material (ESI) for RSC Advances.

Ultrafine $NiMoO_x$ nanoparticles confined in mesoporous carbon for the reduction of nitroarenes: Effect of the composition and accessibility of the active sites

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Table S1. The XPS parameters of Ni 2p and Mo 3d over different catalysts.

Area[d] (%)		Binding energy[b] (eV)			Sample	Binding energy[a] (eV)			Area[c] (%)	
Ni^{2+}	Ni^0	$Ni(OH)_2$	NiO	Ni^0		Mo^0	Mo^{4+}	Mo^{6+}	Mo^0	MoO_x
96.4	3.6	856.2	855	853.0	$NiMoO_x$/MC-PL	230.7	232.4	235.9	22.0	88
82.2	17.8	856.1	854.4	852.9	$NiMoO_x$/MC-PL-450	230.6	232.3	235.5	33.6	66.4
67.5	32.5	856.4	854.5	852.7	$NiMoO_x$/MC-PL-750	230.6	232.3	235.7	36.3	63.7

[a]The binding energy of Mo $3d_{3/2}$.

[b]The binding energy of Ni $2p_{5/2}$.

[c]The difference of valence of Mo species. Area = $Mo^x/(Mo^0 + Mo^{4+}+Mo^{6+})$.

[d]The difference of valence of Ni species. Area = $Ni^x/(Ni^0 + Ni^{2+})$.

Table S2. The kinetic constants and TOF of $NiMoO_x$/MC-PL at different concentration of $NaBH_4$.

Samples	Catalyst amount (mg)	Concentration of $NaBH_4$ ($mol \cdot L^{-1}$)	Concentration of 4-NP ($mol \cdot L^{-1}$)	Time[a] (min)	k (min^{-1})	K ($min^{-1} \cdot g^{-1}$)	TOF[b]$\times 10^3$ (s^{-1})
$NiMoO_x$/MC-PL	0.5	0.005	0.012	8.5	0.10	200	42.6
$NiMoO_x$/MC-PL	0.5	0.01	0.012	6.0	0.19	380	60.4
$NiMoO_x$/MC-PL	0.5	0.02	0.012	2.0	0.48	960	175.8
$NiMoO_x$/MC-PL	0.5	0.03	0.012	2.3	0.41	820	157.5
$NiMoO_x$/MC-PL	0.5	0.04	0.012	1.9	0.49	980	190.7

[a]Calculated at 50% of the conversion.

[b]Calculated on the basis of total catalyst and conversion rate of 50%.

Table S3. The kinetic constants and TOF of $NiMoO_x$/MC-PL under different amount of catalyst in the reduction reaction.

Samples	Catalyst amount (mg)	Concentration of $NaBH_4$ ($mol \cdot L^{-1}$)	Concentration of 4-NP ($mol \cdot L^{-1}$)	Time [a] (min)	k (min^{-1})	K ($min^{-1} \cdot g^{-1}$)	TOF[b]$\times 10^3$ (s^{-1})
$NiMoO_x$/MC-PL	0.0625	0.02	0.012	12.3	0.07	1120	235.6
$NiMoO_x$/MC-PL	0.125	0.02	0.012	7.8	0.12	968	185.8
$NiMoO_x$/MC-PL	0.25	0.02	0.012	4.5	0.27	1080	161
$NiMoO_x$/MC-PL	0.5	0.02	0.012	2.0	0.48	960	175.8
$NiMoO_x$/MC-PL	1.0	0.02	0.012	1.3	1.06	1060	125.5

[a]Calculated at 50% of the conversion.

[b]Calculated on the basis of total catalyst and conversion rate of 50%.

Table S4. The kinetic constants and TOF of $NiMoO_x$/MC-PL under different amount of 4-NP.

Samples	Catalyst amount (mg)	Concentration of $NaBH_4$ ($mol \cdot L^{-1}$)	Amount of 4-NP (μL)	Time[a] (min)	k (min^{-1})	K ($min^{-1} \cdot g^{-1}$)	TOF[b]$\times 10^3$ (s^{-1})
$NiMoO_x$/MC-PL	0.5	0.02	10	1.1	0.77	1540	329.4
$NiMoO_x$/MC-PL	0.5	0.02	15	2.4	0.67	1340	150.9
$NiMoO_x$/MC-PL	0.5	0.02	20	1.8	0.52	1040	201.3
$NiMoO_x$/MC-PL	0.5	0.02	25	2.9	0.46	920	124.9
$NiMoO_x$/MC-PL	0.5	0.02	30	4.3	0.25	500	84.0

[a]Calculated at 50% of the conversion.

[b]Calculated on the basis of total catalyst and conversion rate of 50%.

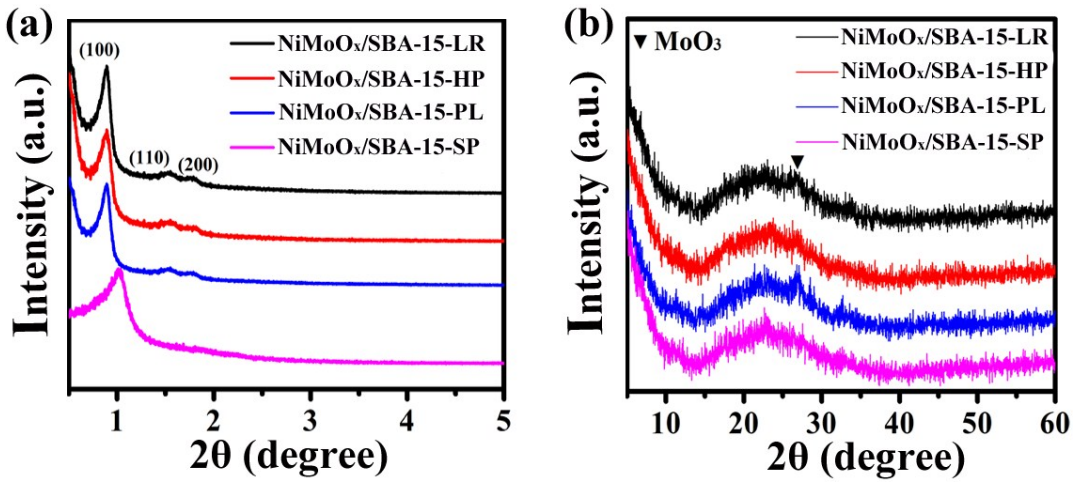

Fig. S1. XRD patterns of various morphologies of $NiMoO_x$/SBA-15 (a, b) in the small-angle and wide-angle.

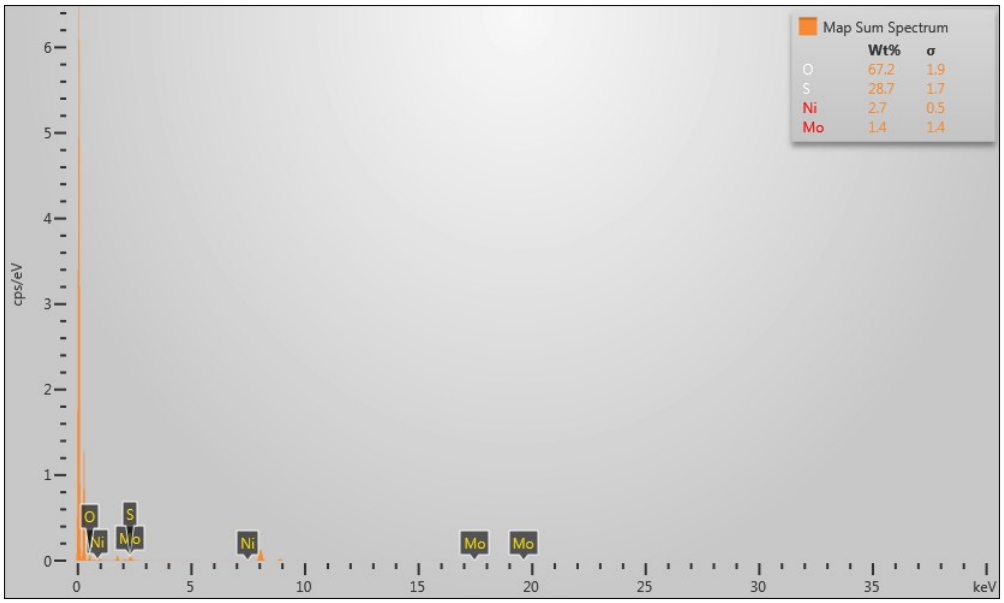

Fig. S2. The EDS analysis of NiMoS/MC-PL.

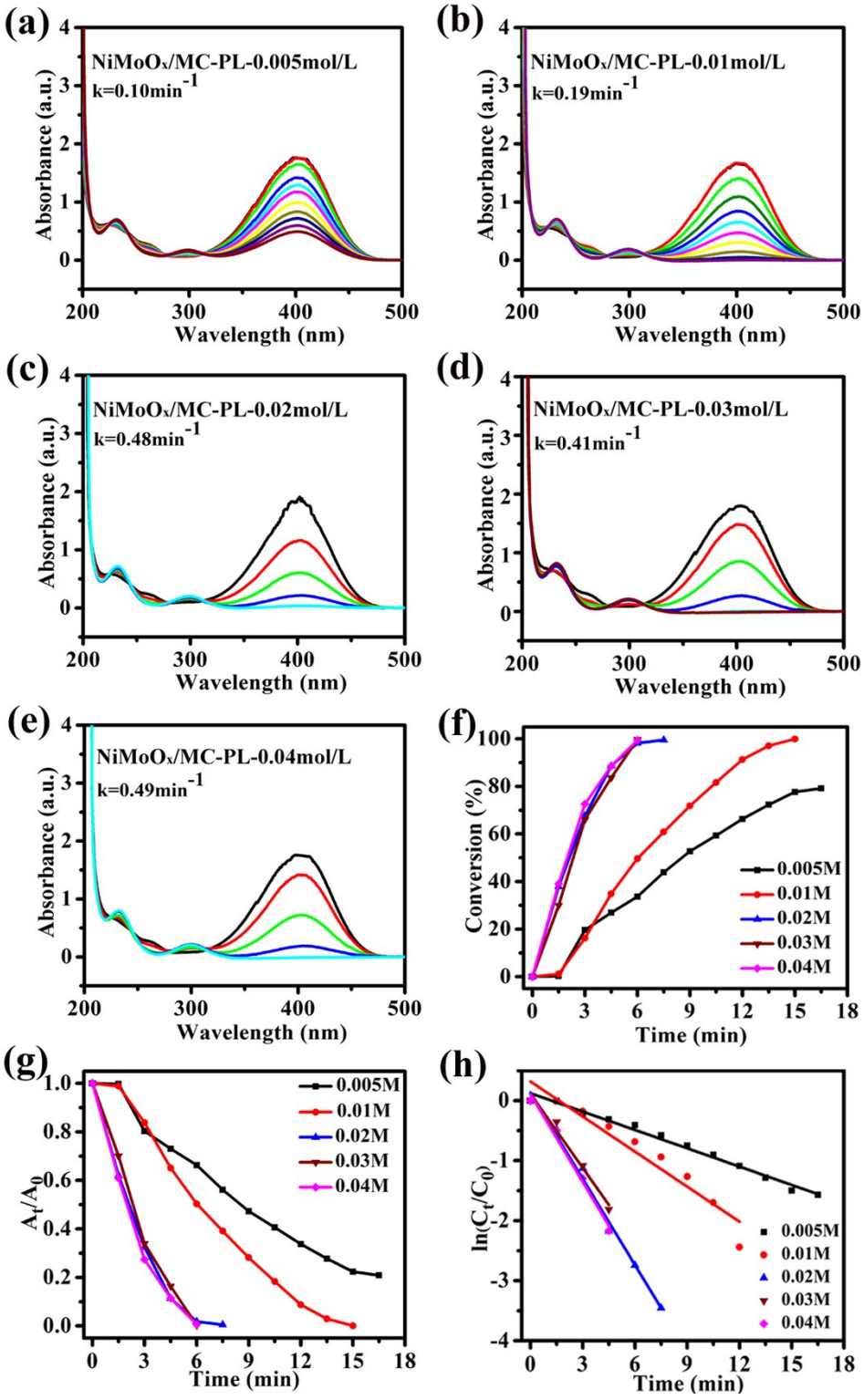

Fig. S3. The reduction of 4-NP recorded every 1.5 min with different concentration of the $NaBH_4$ (a-e); Time dependent conversion of 4-NP over the catalysts (f); The relationship between the A_t/A_0 and reaction time (g); Plots of $\ln(C_t/C_0)$ versus reaction time at different concentration of $NaBH_4$ for reduction 4-NP (h).

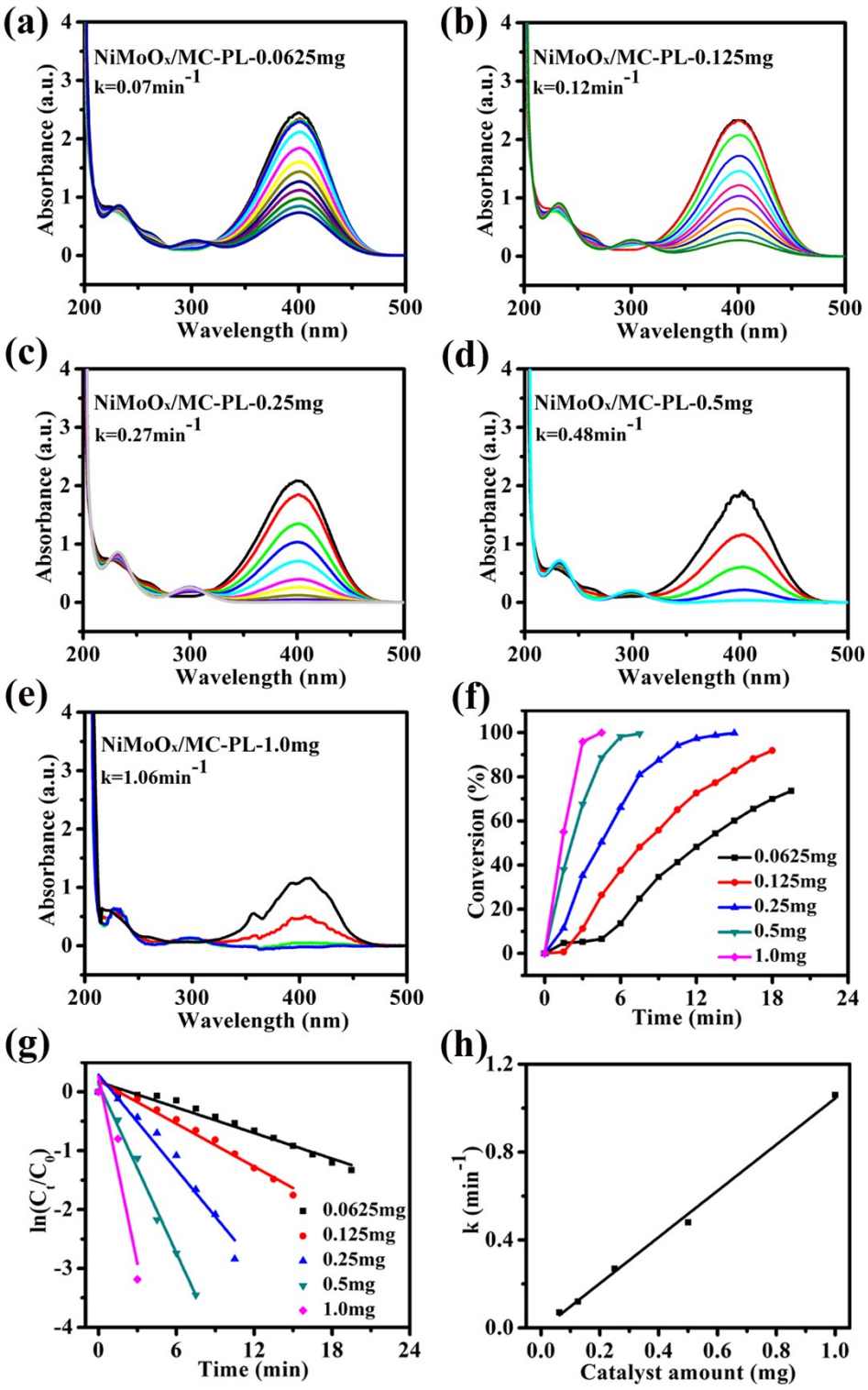

Fig. S4. The reduction of 4-NP recorded every 1.5 min with different amount of catalyst (a-e); Plots of conversion versus time over the different amount of catalyst (f); The relationship between the $\ln(C_t/C_0)$ and reaction time for reduction 4-NP (g); The correlation between the k and amount of catalyst (h).

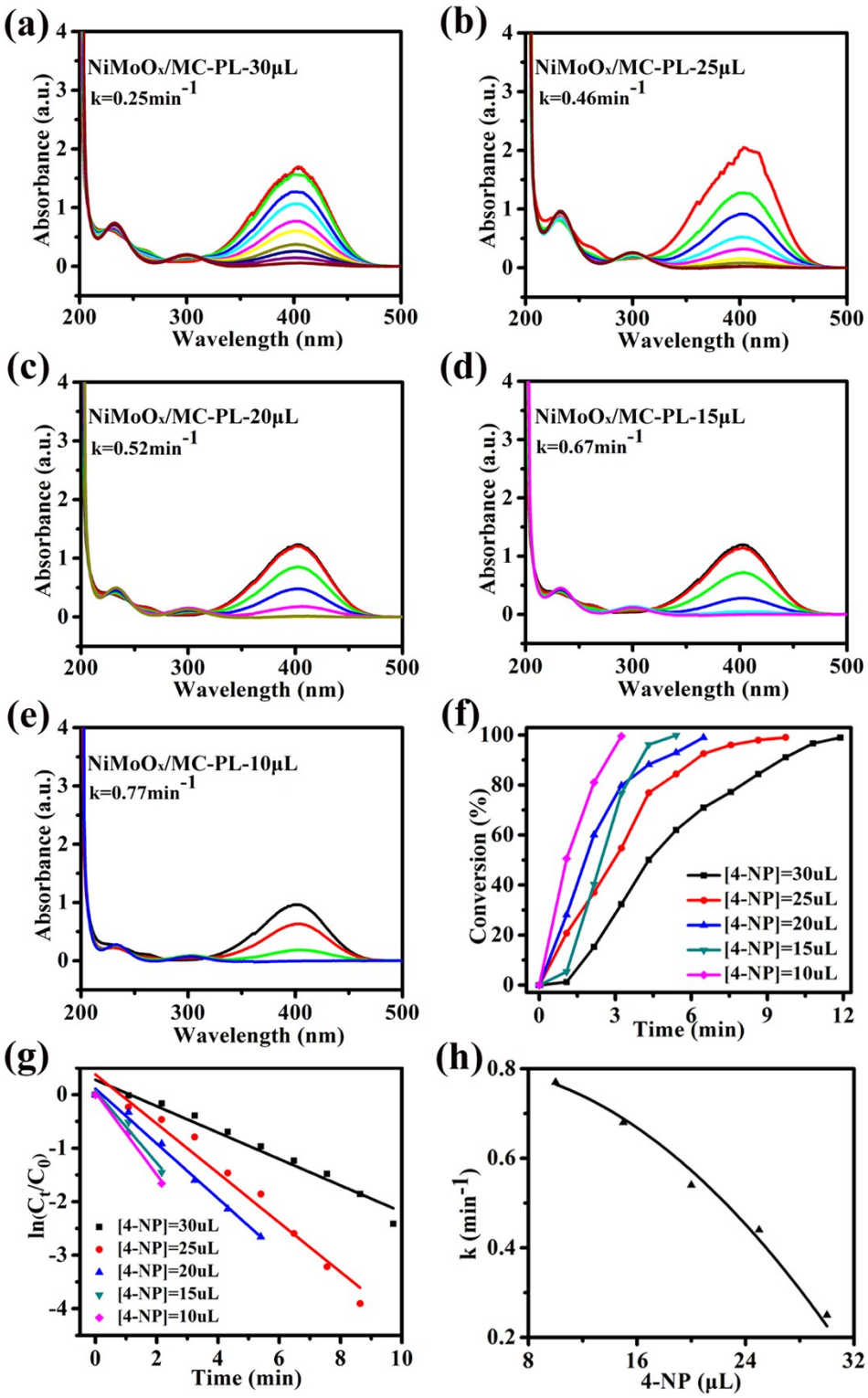

Fig. S5. The reduction of 4-NP recorded every 1.08 min with different amount of 4-NP (a-e); Plots of conversion versus time over the different amount 4-NP (f); The relationship between the $\ln(C_t/C_0)$ and reaction time (g); The correlation between the k and amount of 4-NP (h).