Supplementary Data

For

New Ce-doped MgAl-LDH@Au Nanocatalyst for Highly Efficient Reductive Degradation of Organic Contaminants

Kanwal Iqbal,[a] Anam Iqbal,[a] Alexander M. Kirillov,[b] Bingkai Wang,[a] Weisheng Liu,[a] Yu Tang[a]*

[a] State Key Laboratory of Applied Organic Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou 730000, P.R. China

[b] Centro de Quimica Estrutural, Complexo I, Instituto Superior Técnico, Universidade de Lisboa, Av. Rovisco Pais, Lisbon 1049-001, Portugal

Contents

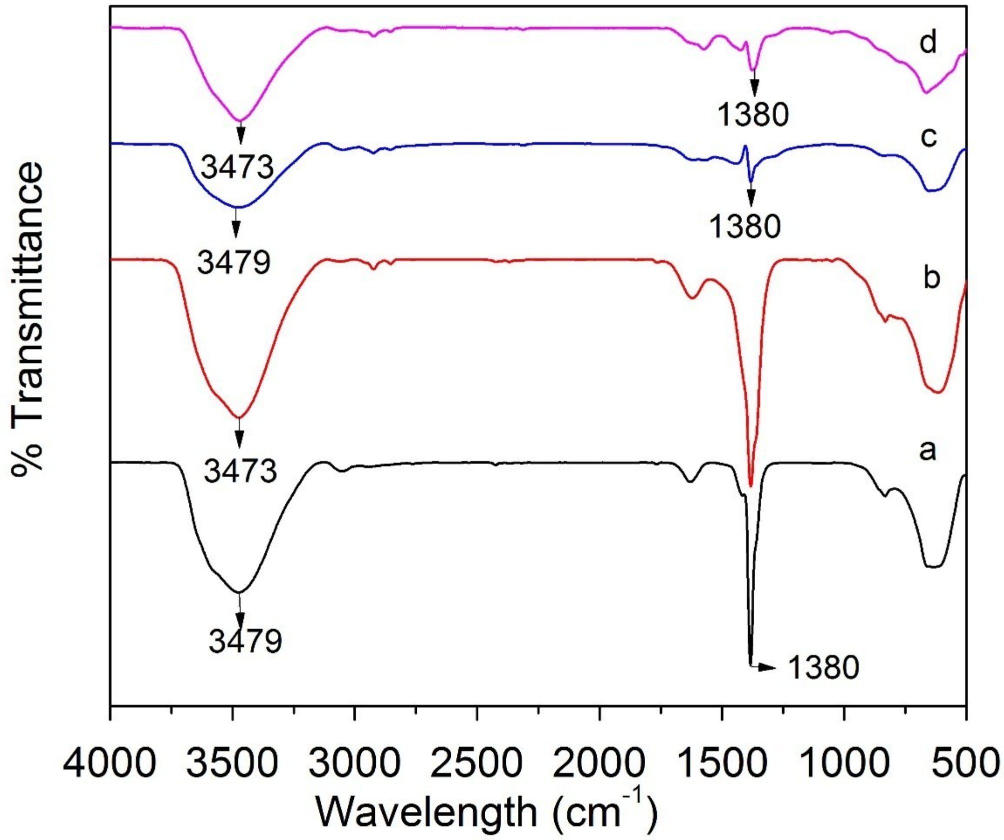

Fig. S1 FT-IR spectra of MgAl-LDH (a), MgAlCe-LDH (b), MgAl-LDH@Au (c), and MgAlCe-LDH@Au (d)

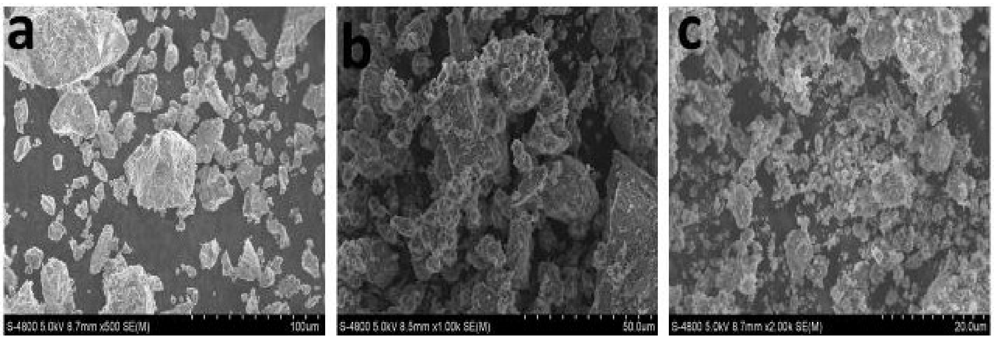

Fig. S2 SEM images of (a) MgAlCe-LDH, (b) MgAl-LDH@Au, and (c) MgAlCe-LDH@Au.

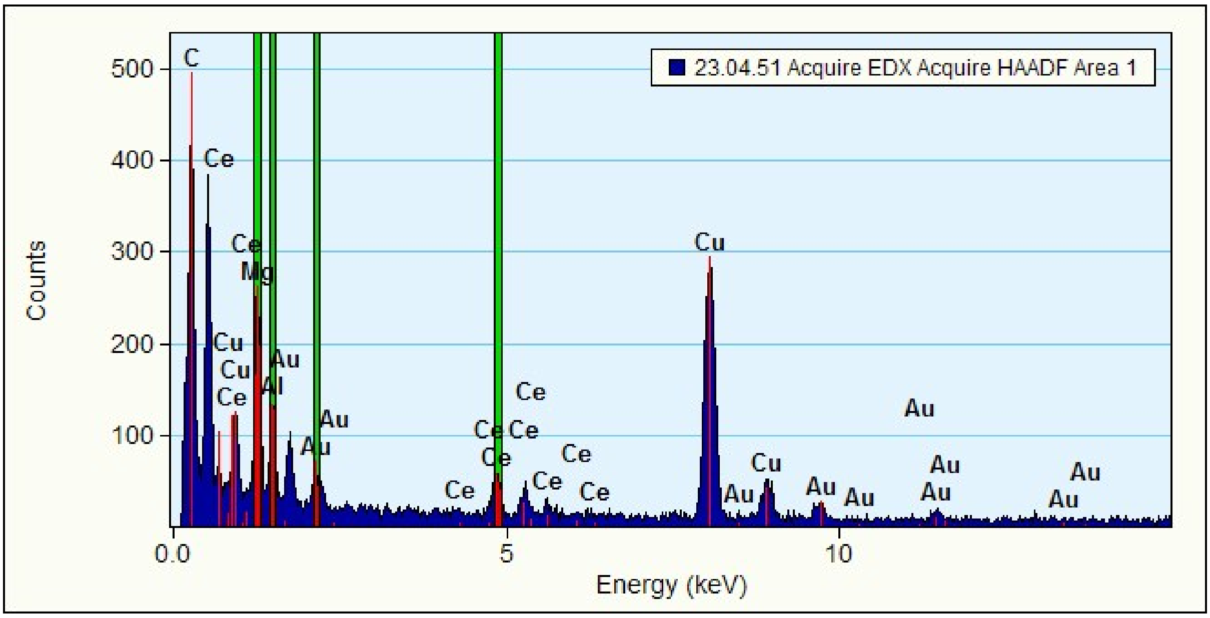

Fig. S3 EDX spectrum of MgAlCe-LDH@Au. The Cu signals originate from Cu grid.

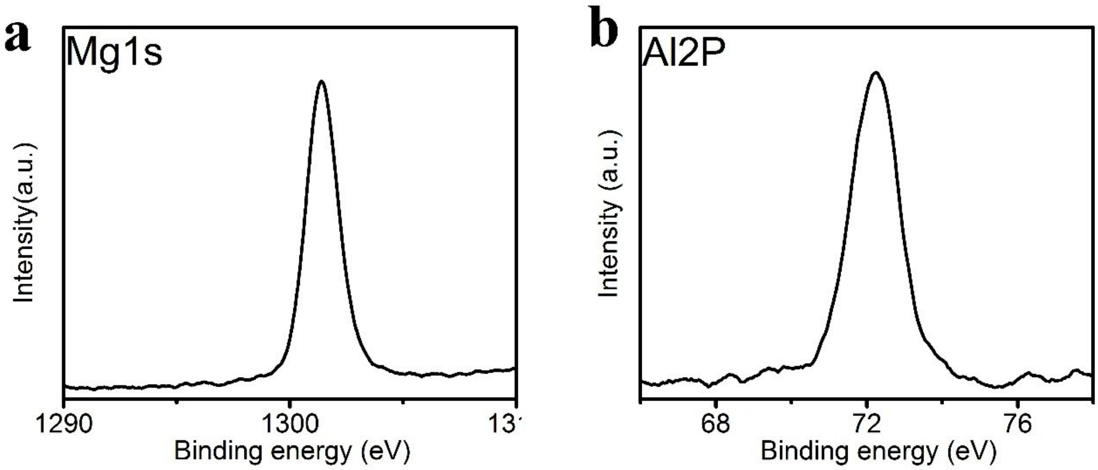

Fig. S4 High-resolution XPS spectra of MgAlCe-LDH@Au: (a) Mg 1s, (b) Al 2p.

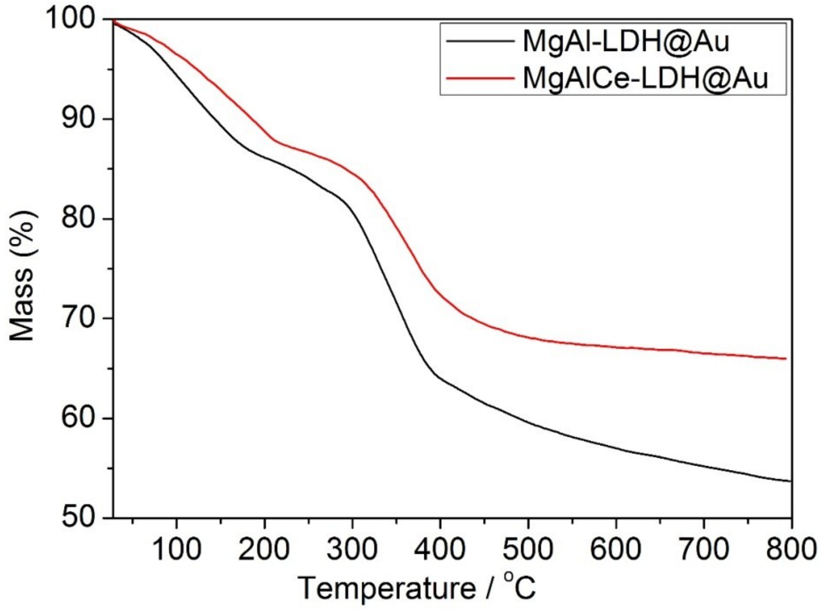

Fig. S5 TGA curves of MgAl-LDH@Au and MgAlCe-LDH@Au.

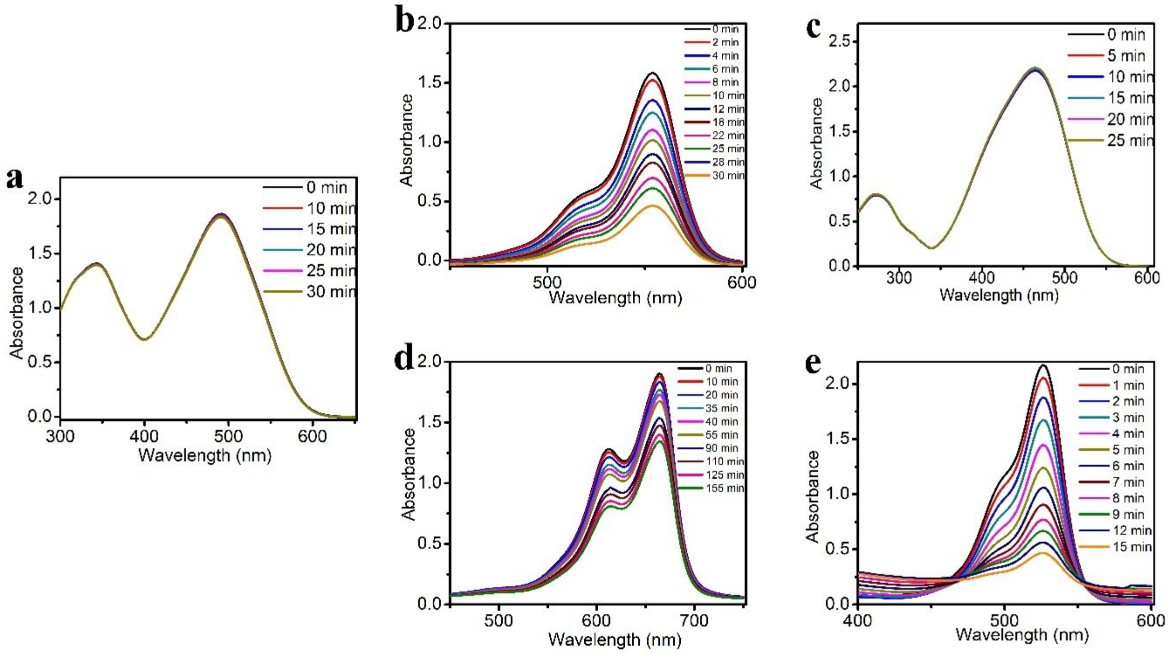

Fig. S6 Time-dependent UV-vis spectra of the reaction mixtures containing (a) CR, (b) RhB, (c) MO, (d) MB, and (e) R6G aqueous solutions in the presence of $NaBH_4$ as a reducing agent and in the absence of catalyst (blank tests). Reaction conditions: 2.5 mL aqueous solutions of (a) CR (6×10^{-5} M), (b) RhB (2×10^{-6} M), (c) MO (1×10^{-4} M), (d) MB (3×10^{-5} M), (e) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 480 μL).

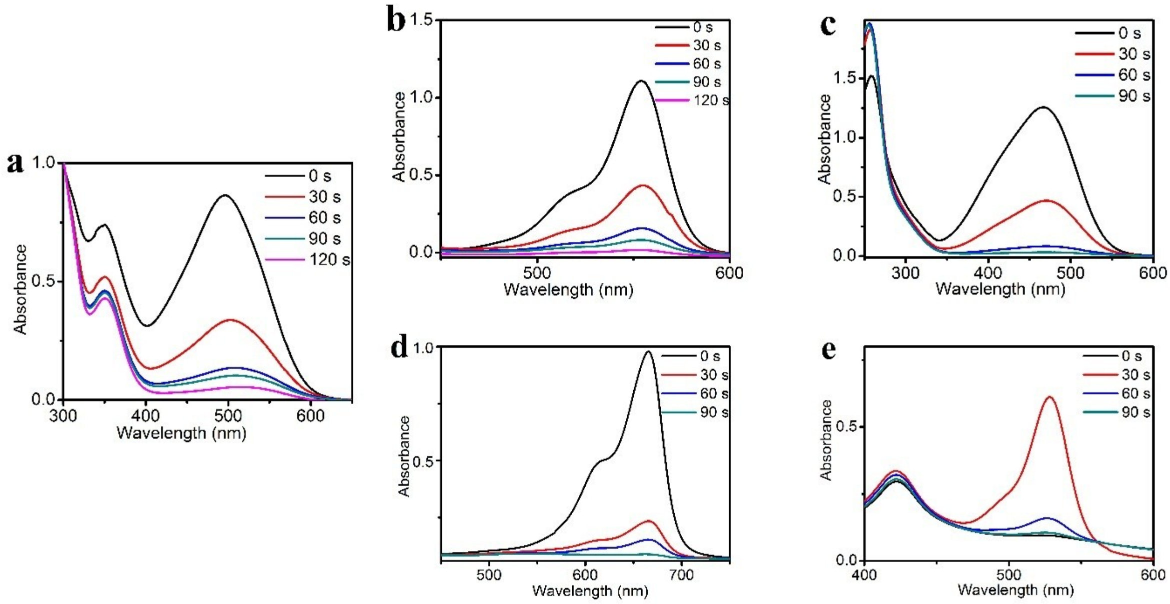

Fig. S7 Time-dependent UV-vis spectra of the reaction mixtures containing (a) CR, (b) RhB, (c) MO, (d) MB, and (e) R6G aqueous solutions in the presence of $NaBH_4$ as a reducing agent and MgAlCe-LDH@Au as a catalyst. Reaction conditions: MgAlCe-LDH@Au (20 μL, 1 mg/mL), 2.5 mL aqueous solutions of (a) CR (6×10^{-5} M), (b) RhB (2×10^{-6} M), (c) MO (1×10^{-4} M), (d) MB (3×10^{-5} M), (e) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 480 μL).

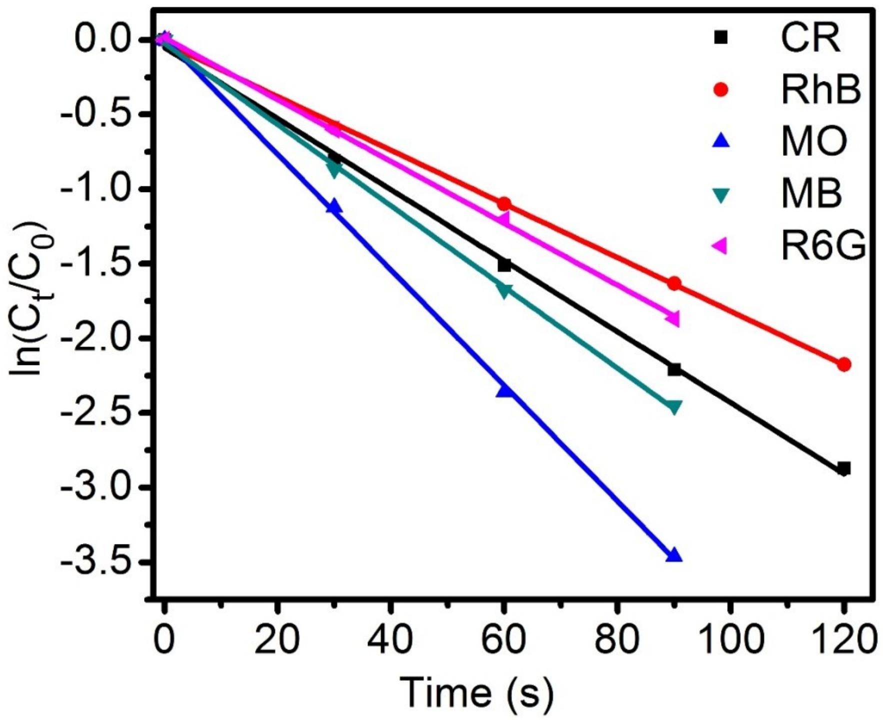

Fig. S8 Calibration curves as a function of ln(C_t/C_0) *vs*. reaction time for the reaction mixtures containing aqueous solutions of dyes (a) CR, (b) RhB, (c) MO, (d) MB, and (e) R6G in the presence of $NaBH_4$ as a reducing agent and MgAlCe-LDH@Au (20 µL, 1 mg/mL) as a catalyst. Reaction conditions: MgAlCe-LDH@Au (20 µL, 1 mg/mL), 2.5 mL aqueous solutions of (a) CR (6×10^{-5} M), (b) RhB (2×10^{-6} M), (c) MO (1×10^{-4} M), (d) MB (3×10^{-5} M), (e) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 480 µL).

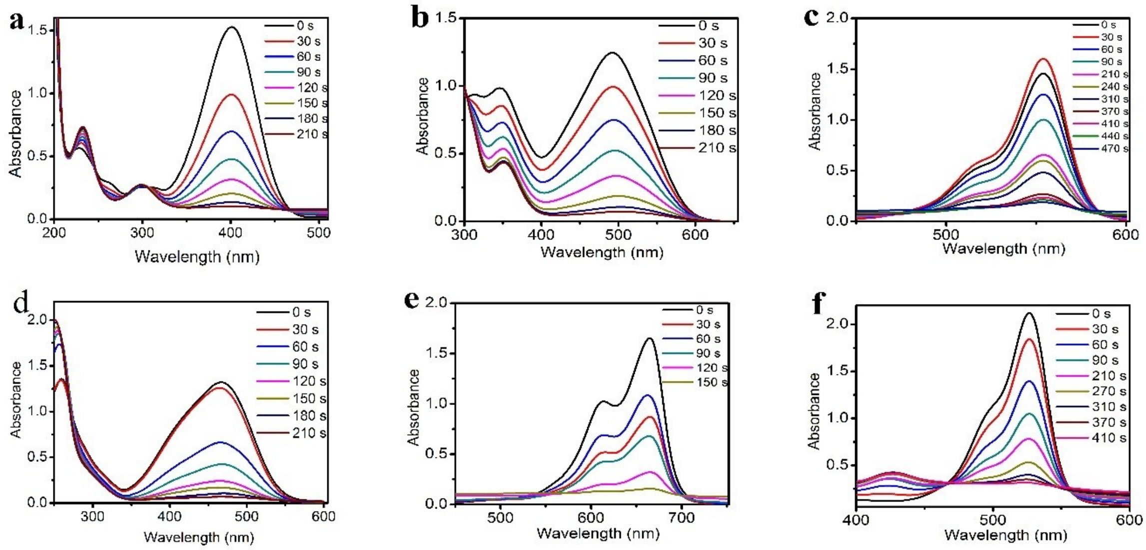

Fig. S9 Time-dependent UV-vis spectra of the reaction mixtures containing (a) 4-NP, (b) CR, (c) RhB, (d) MO, (e) MB and (f) R6G aqueous solutions in the presence of $NaBH_4$ as a reducing agent and MgAl-LDH@Au as a catalyst. Reaction conditions: MgAl-LDH@Au (20 μL, 1 mg/mL), 2.5 mL aqueous solutions of (a) 4-NP (10 mM) (b) CR (6×10^{-5} M), (c) RhB (2×10^{-6} M), (d) MO (1×10^{-4} M), (e) MB (3×10^{-5} M), (f) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 200 μL for 4-NP and 480 μL for dyes).

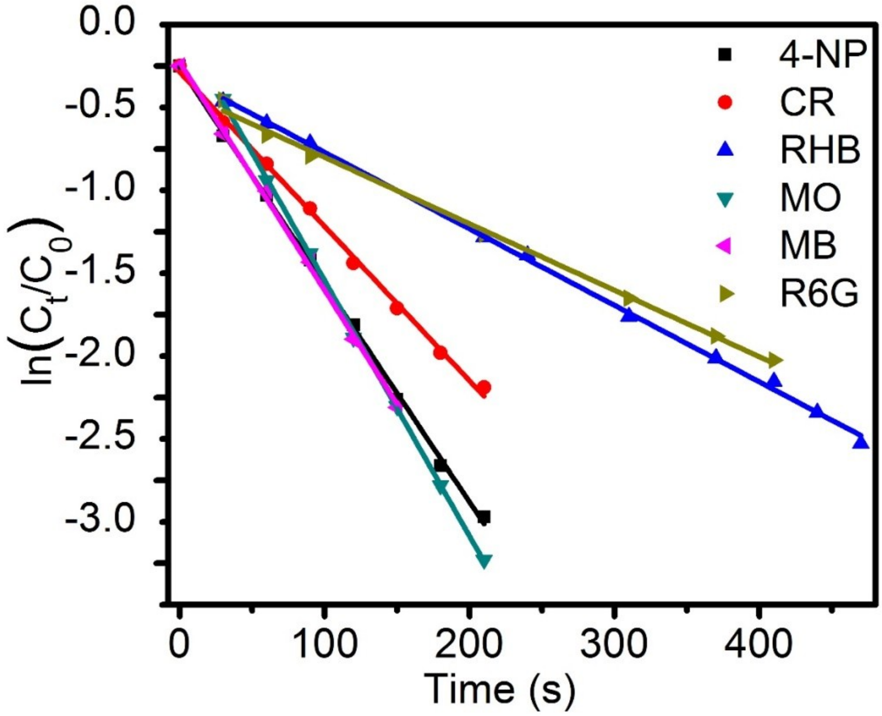

Fig. S10 Calibration curves as a function of ln(C_t/C_0) *vs.* reaction time for the reaction mixtures containing (a) 4-NP, (b) CR, (c) RhB, (d) MO, (e) MB and (f) R6G aqueous solutions in the presence of $NaBH_4$ as a reducing agent and MgAl-LDH@Au as a catalyst. Reaction conditions: MgAl-LDH@Au (20 µL, 1 mg/mL), 2.5 mL aqueous solutions of (a) 4-NP (10mM) (b) CR (6×10^{-5} M), (c) RhB (2×10^{-6} M), (d) MO (1×10^{-4} M), (e) MB (3×10^{-5} M), (f) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 200 µL for 4-NP and 480 µL for dyes).

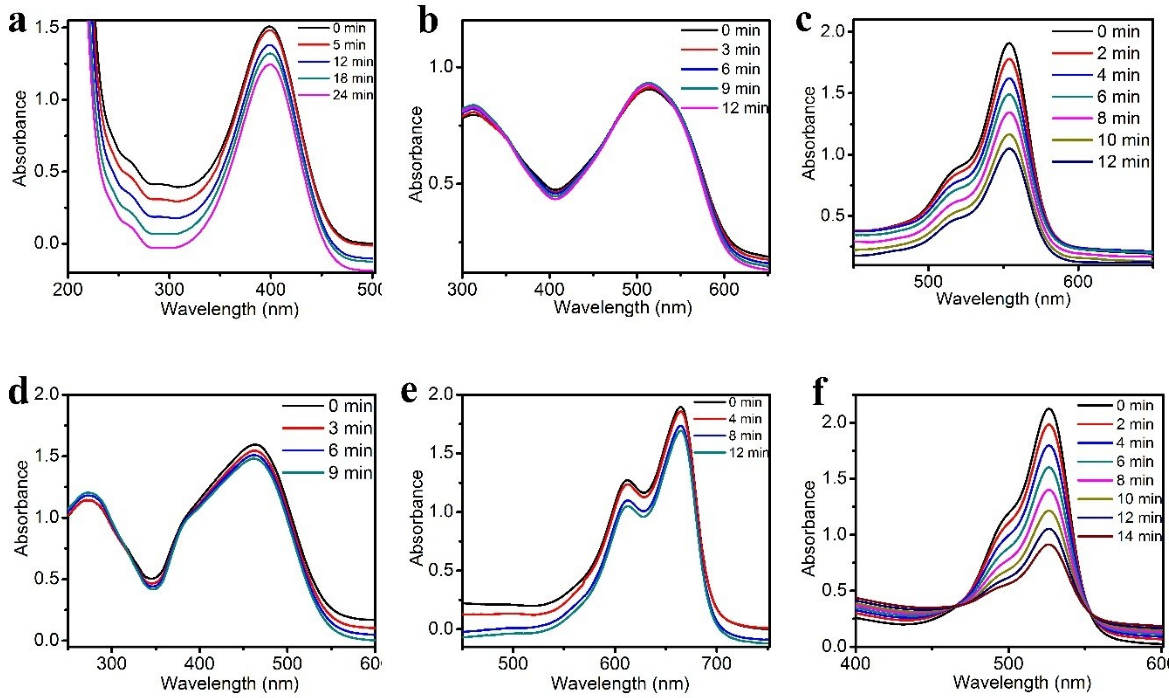

Fig. S11 Time-dependent UV-vis spectra of the reaction mixtures containing (a) 4-NP, (b) CR, (c) RhB, (d) MO, (e) MB and (f) R6G aqueous solutions in the presence of $NaBH_4$ as a reducing agent and MgAlCe-LDH as a catalyst. Reaction conditions: MgAlCe-LDH (20 µL, 1 mg mL^{-1}), 2.5 mL aqueous solutions of (a) 4-NP (10 mM), (b) CR (6×10^{-5} M), (c) RhB (2×10^{-6} M), (d) MO (1×10^{-4} M), (e) MB (3×10^{-5} M), (f) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 200 µL for 4-NP and 480 µL for dyes).

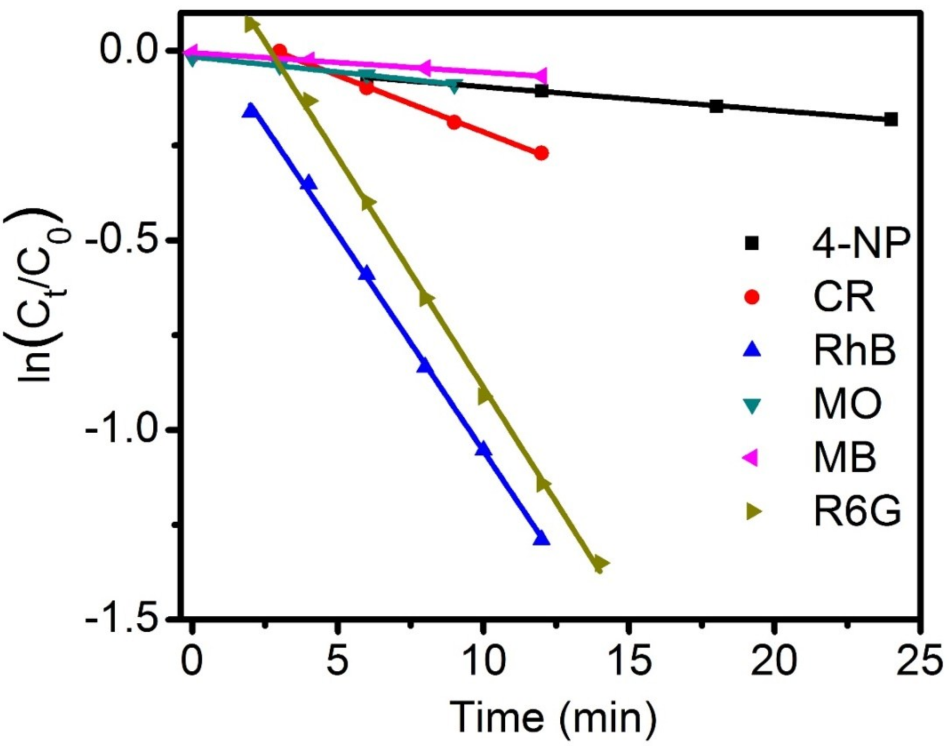

Fig. S12 Calibration curves as a function of ln(C_t/C_0) *vs.* reaction time for the reaction mixtures containing (a) 4-NP, (b) CR, (c) RhB, (d) MO, (e) MB, and (f) R6G aqueous solutions in the presence of $NaBH_4$ as a reducing agent and MgAlCe-LDH as a catalyst. Reaction conditions: MgAlCe-LDH (20 µL, 1 mg/mL), 2.5 mL aqueous solutions of (a) 4-NP (10 mM), (b) CR (6×10^{-5} M), (c) RhB (2×10^{-6} M), (d) MO (1×10^{-4} M), (e) MB (3×10^{-5} M), (f) R6G (4×10^{-4} M), and $NaBH_4$ (0.1 M, 200 µL for 4-NP and 480 µL for dyes).

Table S1 Comparison of various catalytic systems for the reductive degradation of 4-NP.

Catalyst	**Support**	**Reaction time (s)**	$\mathbf{k_{app}}$ **(S^{-1})**	**TOF (h^{-1})**	**Reference**
Au doped meso-porous Boehmite film	Boehmite film	1920	1.7×10^{-3}	0.7	S1
PANI nanofiber/Au NPs	PANI	300	11.7×10^{-3}	0	S2
AuNPs/SNTs nanocomposite	SNTs	280	10.6×10^{-3}	46	S3
AuNPs@CSNFs	CSNFs	960	5.9×10^{-3}	563	S4
Au@HSNs_C	SiO_2	1800	1.0×10^{-3}	14	S5
AuNPs@ZnO paper	Hydrogel ZnO	240	2.4×10^{-3}	3	S6
Hollow capsule-stabilized Ag NPs	PAMAM	1800	2.0×10^{-3}	196	S7
SiO_2@Au/CeO_2	SiO_2@CeO_2	300	1.3×10^{-2}	240	S8
Micelle-supported Ag NPs	PNIPAP-b-P4VP	1950	1.5×10^{-3}	16	S9
Au-DEND550-1	Au-DEND-PEG550	350	9.4×10^{-3}	901	S10
Au(0)@TpPa-1	Au(0)@TpTa-1	780	5.4×10^{-3}	9	S11
An NPNs	Peptide	300	1.3×10^{-3}	7	S12
α-CDS capped Au NPs	α-CD	600	4.7×10^{-3}	34	S13
Au/graphene hydrogel	Graphene	720	3.2×10^{-3}	12	S14
Au NPs	HPEI-IBAm	1140	-	120	S15
Au NPs/TWEEN/GO composites	TWEEN/GO	840	4.2×10^{-3}	7	S16
Au-EGCG$_{0.1}$-CF	EGCG-CF	1800	2.4×10^{-3}	2	S17
DMF-stabilized Au NCs	DMF	4200	3.0×10^{-3}	83	S18
Magnetically recoverable Au nanocatalyst	Chitosan	600	1.2×10^{-2}	50	S19
Au-composite NPs	PDMAEMA-PS	750	3.2×10^{-3}	1	S20
Pt1Au1-RGO	PDA/RGO	1800	0.7×10^{-3}	14	S21
Pt3Au1-PDA/RGO	PDA/RGO	600	9.6×10^{-3}	200	S21
Pt1Au1-PDA/RGO	PDA/RGO	600	5.7×10^{-3}	118	S21
Au-PDA/RGO	PDA/RGO	600	2.0×10^{-3}	42	S21
Au NPs	Solution B	120	2.0×10^{-2}	3.0×10^{3}	S22
Au NPs	Solution B	200	9.0×10^{-3}	9.0×10^{3}	S22
Au NPs	Solution B	1320	1.0×10^{-3}	5.5×10^{3}	S22
Fe_3O_4@CTS-Au NPs(A)	Fe_3O_4	1320	8.6×10^{-3}	272	S23
Fe_3O_4@CTS-Au NPs(G)	Fe_3O_4	1320	1.7×10^{-2}	296	S23
Fe_3O_4@C16@CTS-Au NPs(A)	Fe_3O_4	1320	2.2×10^{-2}	413	S23
Fe_3O_4@C16@CTS-Au NPs(G)	Fe_3O_4	100	3.1×10^{-2}	440	S23
MgAl-LDH@Au	**MgAl-LDH**	**210**	$\mathbf{1.3 \times 10^{-2}}$	$\mathbf{3.4 \times 10^{5}}$	**This work**
MgAlCe-LDH@Au	**MgAlCe-LDH**	**60**	$\mathbf{4.1 \times 10^{-2}}$	$\mathbf{1.2 \times 10^{6}}$	**This work**

Table S2 Comparison of various catalytic systems for the reductive degradation of dyes: methylene blue (MB), methyl orange (MO), Congo red (CR), rhodamine B (RhB), and rhodamine 6G (R6G).

Catalyst	**Support**	**Dye**	**Dye concentration**	**Reaction time (s)**	k_{app} **(s^{-1})**	**TOF (h^{-1})**	**Reference**
sFe_3O_4@C16@CTS-Au NPs(G)	Fe_3O_4	MB	3.0×10^{-5} M	100	3.0×10^{-8}	114	S23
Au Nps/MCNSC	CNSs	MB	1 mM	720	3.3×10^{-3}	0	S24
Fe_3O_4@C@Au Nps	Fe_3O_4@C	MB	1.0×10^{-7} M	600	5.0×10^{-3}	0	S25
Au@TA-GH	Graphene	MB	0.63 µM	540	2.0×10^{-3}	26	S26
Au NPs	P.benghalensis	MB	10 mg mL^{-1}	480	2.9×10^{-3}	-	S27
Au/$KNbO_3$	$KNbO_3$	MB	4.0×10^{-5} M	7200	2.0×10^{-4}	0.05	S28
Au NPs	S.acuminata fruit extract	MB	10^{-4} N	720	7.0×10^{-4}	0	S29
Au NPs	Kashayam	MB	9.4×10^{-5} M	300	5.5×10^{-3}	0	S30
Au NPs	Punica granatum	MB	1 mM	900	6.0×10^{-3}	0	S28
MgAlCe-LDH@Au	**MgAlCe-LDH**	**MB**	**3.0×10^{-5} M**	**90**	**3×10^{-3}**	**2.2×10^{3}**	**This work**
Fe_3O_4@C16@CTS-Au NPs(G)	Fe_3O_4	MO	1.0×10^{-4} M	120	2.0×10^{-2}	304	S23
Au NPs	Punica granatum	MO	1 mM	900	3.0×10^{-3}	0	S28
Au NPs	S.acuminata fruit extract	MO	10^{-4} N	720	6.0×10^{-4}	0	S30
MgAlCe-LDH@Au	**MgAlCe-LDH**	**MO**	**1.0×10^{-4} M**	**90**	**4.0×10^{-2}**	**8.0×10^{3}**	**This work**
Fe_3O_4@C16@CTS-Au NPs(G)	Fe_3O_4	CR	6.0×10^{-5} M	150	1.3×10^{-2}	149	S19
MgAlCe-LDH@Au	**MgAlCe-LDH**	**CR**	**6.0×10^{-5} M**	**120**	**2.4×10^{-2}**	**3.3×10^{3}**	**This work**
Fe_3O_4@C16@CTS-Au NPs(G)	Fe_3O_4	RhB	2.0×10^{-6} M	140	1.6×10^{-2}	4.8	S19
MgAlCe-LDH@Au	**MgAlCe-LDH**	RhB	**2.0×10^{-6} M**	**120**	**2.0×10^{-2}**	**111**	**This work**
Fe_3O_4@C16@CTS-Au NPs(G)	Fe_3O_4	R6G	4.0×10^{-4} M	240	1.0×10^{-2}	626	S19
MgAlCe-LDH@Au	**MgAlCe-LDH**	**R6G**	**4.0×10^{-4} M**	**90**	**2.1×10^{-2}**	**2.9×10^{4}**	**This work**

Supplementary References

S1. D. Jana, A. Dandapat and G. De, Langmuir., 2010, 26, 12177-12184.
S2. J. Han, L. Li and R. Guo, Macromolecules., 2010, 43, 10636-10644.
S3. Z. Zhang, C. Shao, P. Zou, P. Zhang, M. Zhang, J. Mu, Z. Guo, X. Li, C. Wang and Y. Liu, Chem. Commun., 2011, 47, 3906-3908.
S4. H. Koga, E. Tokunaga, M. Hidaka, Y. Umemura, T. Saito, A. Isogai and T. Kitaoka, Chem. Commun., 2010, 46, 8567-8569.
S5. S.-H. Wu, C.-T. Tseng, Y.-S. Lin, C.-H. Lin, Y. Hung and C.-Y. Mou, J. Mater. Chem., 2011, 21, 789-794.
S6. H. Koga and T. Kitaoka, Chem. Eng. J., 2011, 168, 420-425.
S7. H. Wu, Z. Liu, X. Wang, B. Zhao, J. Zhang and C. Li, J. Colloid. Interf. Sci., 2006, 302, 142-148.
S8. B. Liu, S. Yu, Q. Wang, W. Hu, P. Jing, Y. Liu, W. Jia, Y. Liu, L. Liu and J. Zhang, Chem. Commun., 2013, 49, 3757-3759.
S9. Y. Wang, G. Wei, W. Zhang, X. Jiang, P. Zheng, L. Shi and A. Dong, J. Mater. Chem. A., 2007, 266, 233-238.
S10. N. Li, M. Echeverria, S. Moya, J. Ruiz and D. Astruc, Inorg. Chem., 2014, 53, 6954-6961.
S11. P. Pachfule, S. Kandambeth, D. D. Díaz and R. Banerjee, Chem. Commun., 2014, 50, 3169-3172.
S12. R. Bhandari and M. R. Knecht, Catal. Sci.Technol., 2012, 2, 1360-1366.
S13. T. Huang, F. Meng and L. Qi, J. Phys. Chem. C., 2009, 113, 13636-13642.
S14. J. Li, C.-y. Liu and Y. Liu, J. Mater. Chem., 2012, 22, 8426-8430.
S15. X.-Y. Liu, F. Cheng, Y. Liu, H.-J. Liu and Y. Chen, J. Mater. Chem., 2010, 20, 360-368.
S16. W. Lu, R. Ning, X. Qin, Y. Zhang, G. Chang, S. Liu, Y. Luo and X. Sun, J.Hazard. Mater., 2011, 197, 320-326.
S17. H. Wu, X. Huang, M. Gao, X. Liao and B. Shi, Green. Chem., 2011, 13, 651-658.
S18. H. Yamamoto, H. Yano, H. Kouchi, Y. Obora, R. Arakawa and H. Kawasaki, Nanoscale., 2012, 4, 4148-4154.
S19. Y.-C. Chang and D.-H. Chen, J.Hazard. Mater., 2009, 165, 664-669.
S20. M. Zhang, L. Liu, C. Wu, G. Fu, H. Zhao and B. He, Polymer., 2007, 48, 1989-1997.
S21. W. Ye, J. Yu, Y. Zhou, D. Gao, D. Wang, C. Wang and D. Xue Appl. Catal. B Environ., 2016, 181, 371-378.
S22. C. Deraedt, L. Salmon, S. Gatard, R. Ciganda, R. Hernandez, J. Ruiz and D. Astruc, Chem. Commun., 2014, 50, 14194-14196.
S23. J. Hu, Y.-l. Dong, Z. ur Rahman, Y.-h. Ma, C.-l. Ren and X.-g. Chen, Chem. eng. J., 2014, 254, 514-523.
S24. W. Zuo, G. Chen, F. Chen, S. Li and B. Wang, RSC. Adv., 2016, 6, 28774-28780.
S25. Z. Gan, A. Zhao, M. Zhang, W. Tao, H. Guo, Q. Gao, R. Mao and E. Liu, Dalton Trans., 2013, 42, 8597-8605.
S26. J. Luo, N. Zhang, J. Lai, R. Liu and X. Liu, J. Hazard. Mater., 2015, 300, 615-623.
S27. B. Paul, B. Bhuyan, D. D. Purkayastha, M. Dey and S. S. Dhar, Mater. Lett., 2015, 148, 37-40.
S28. L. Yan, T. Zhang, W. Lei, Q. Xu, X. Zhou, P. Xu, Y. Wang and G. Liu, Catal. Today., 2014, 224, 140-146.
S29. V. Suvith and D. Philip, Spectrochim. Acta A Mol. Biomol.Spectrosc., 2014, 118, 526-532.
S30. M. MeenaKumari and D. Philip, Spectrochim. Acta A Mol. Biomol.Spectrosc., 2015, 135, 632-638.