Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Size-selective adsorption of anionic dyes induced by layer space on layered double hydroxides hollow microspheres

Peipei Huang[a, b], Jian Liu[a, b], Fang Wei[a, b], Yanan Zhu[a, b], Xiaoshi Wang[a, b], Changyan Cao[*a, b] and Weiguo Song[*a, b]

Received (in XXX, XXX) XthXXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

[a]*Beijing National Laboratory for Molecular Sciences (BNLMS)& Key Laboratory of Molecular Nanostructure and Nanotechnology, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, People's Republic of China*
E-mail: cycao@iccas.ac.cn, wsong@iccas.ac.cn.
[b]*University of Chinese Academy of Sciences, Beijing 100049, People's Republic of China*

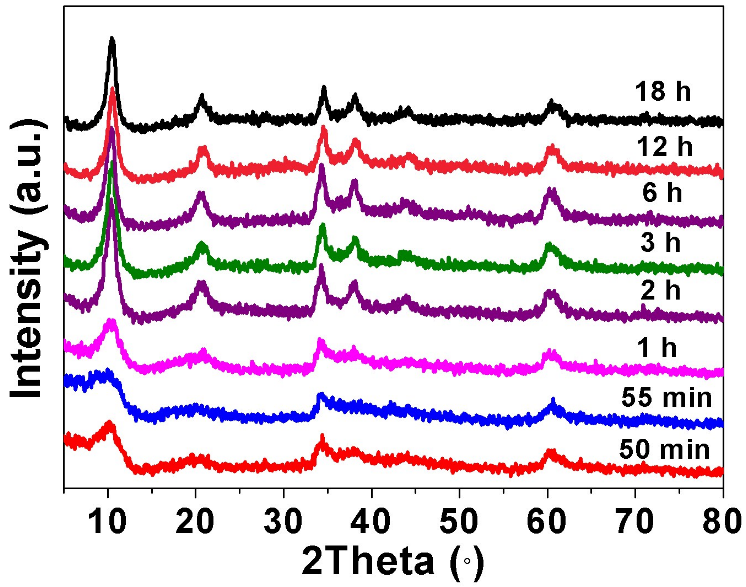


Fig. S1 XRD patterns of samples derived from the time dependent experiments

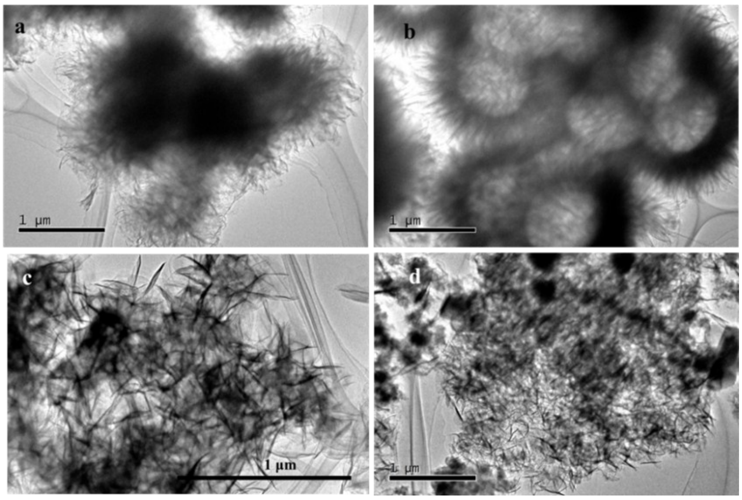


Fig. S2 TEM images of samples derived from different amounts of NH_4F added, (a) 0 g, (b) 0.2 g, (c) 0.4 g and (d) 0.8 g

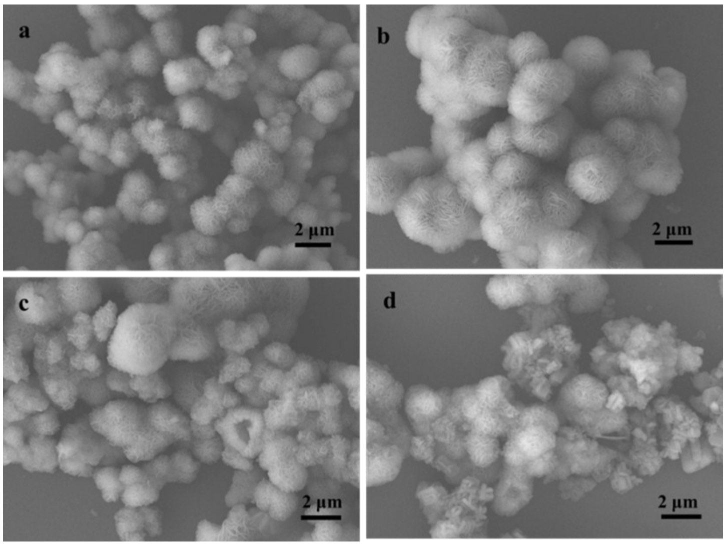


Fig.S3 SEM images of samples derived from different amounts of NH_4F added, (a) 0 g, (b) 0.2 g, (c) 0.4 g and (d) 0.8 g

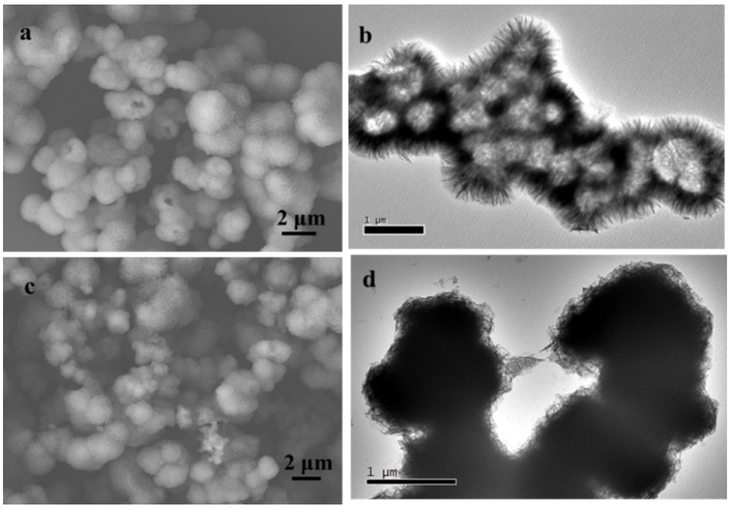


Fig. S4 SEM and TEM images of samples derived from NaF (a) and (b), NH_4Cl (c) and (d), respectively

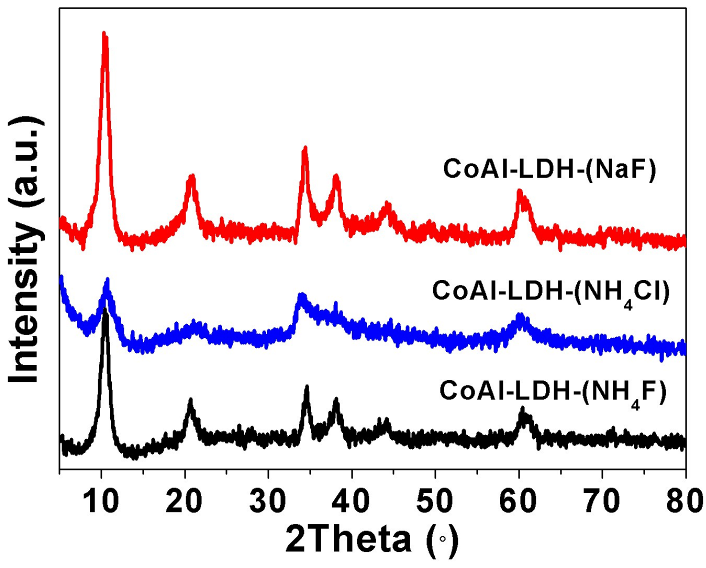


Fig. S5 XRD patterns of the samples prepared in the presence of NaF, NH_4Cl and NH_4F

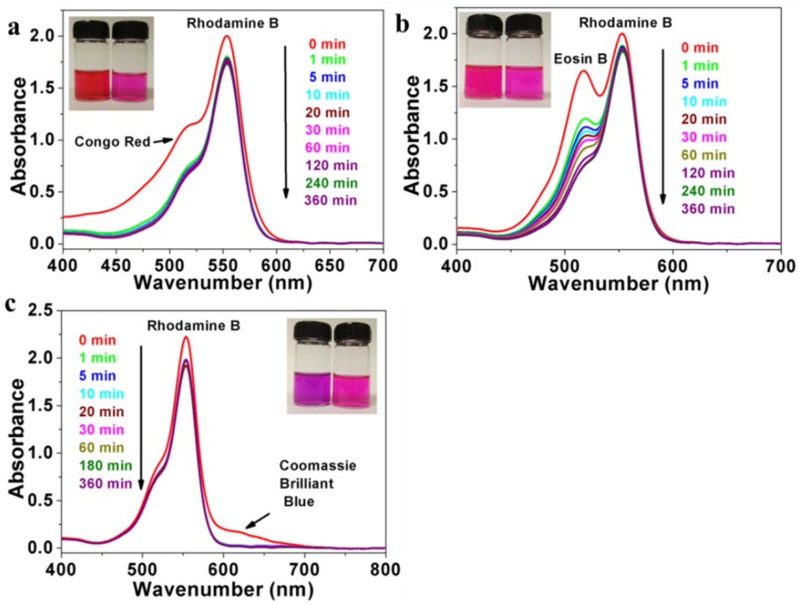


Fig. S6 UV-Vis spectral changes of 100 ml 10 ppm dye mixture in the presence of 20 mg flower-like CoAl-LDHs hollow spheres. (a) Congo Red & Rhodamine B; (b) Eosin B & Rhodamine B; (c) Coomassie Brillant Blue & Rhodamine B. The inset photographs are before (left) and after adsorption (right).

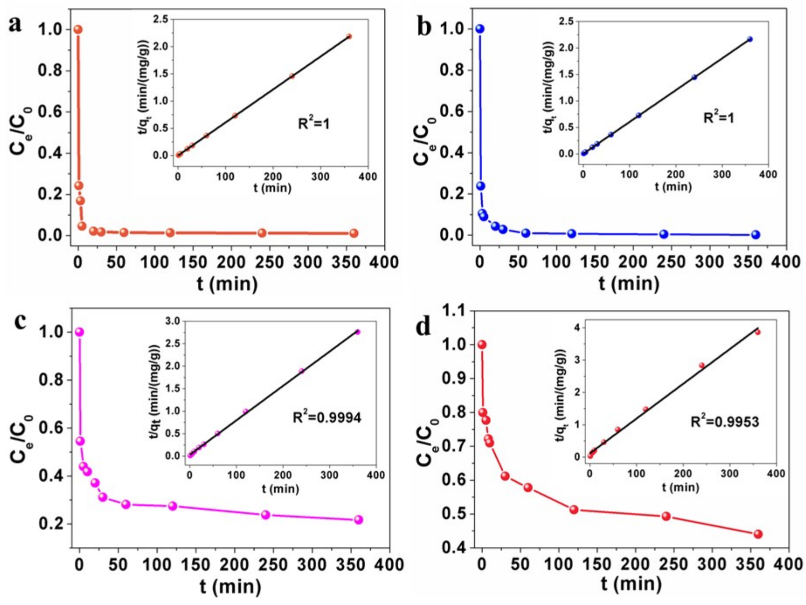


Fig. S7 Adsorption rates of Methyl Orange (a), Coommassie Brilliant Blue (b), Congo Red (c) and Eosin B (d) on the CoAl-LDHs hollow microspheres and all the initial concentration of dye molecules was 100 $mg{\cdot}L^{-1}$. The insets show the corresponding pseudo-second-order kinetics model.

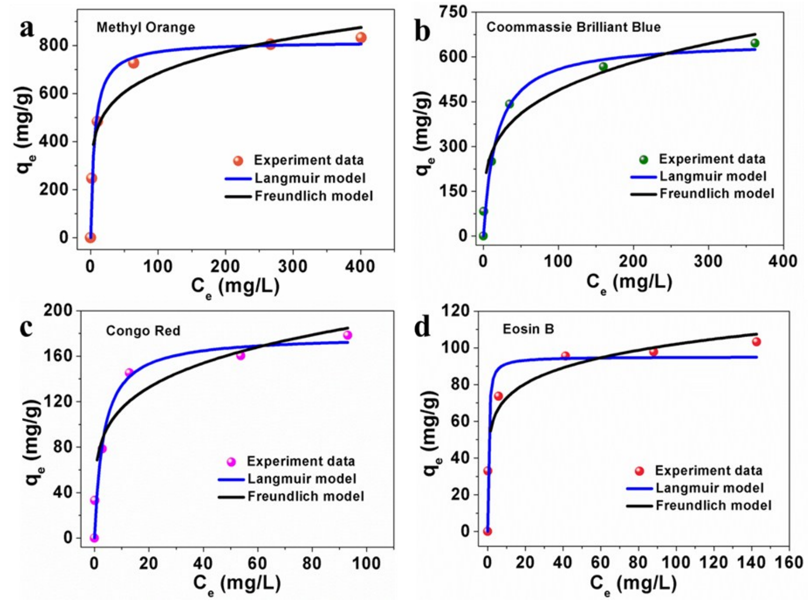


Fig. S8 Adsorption isotherm curves of Methyl Orange (a), Coommassie Brilliant Blue (b), Congo Red (c) and Eosin B (d) on the flower-like CoAl-LDHs hollow microspheres.

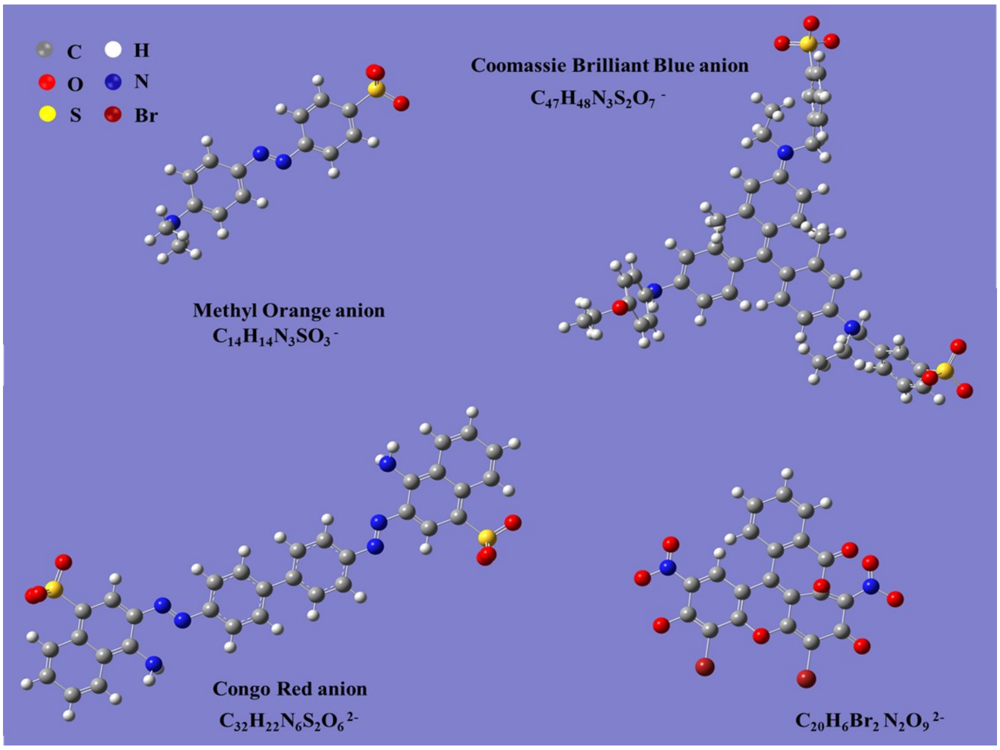


Fig. S9 3D molecular schematic illustrations (Drew by GaussView 5.0) of four anionic dyes

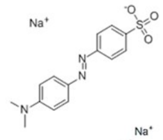
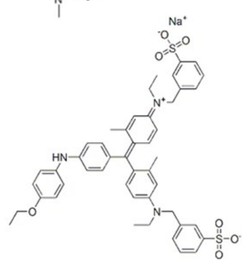
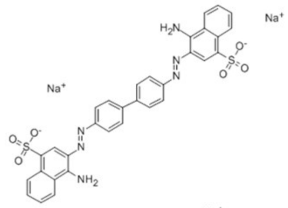
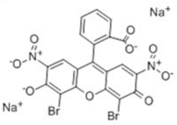
Table S1 Summary of the Langmuir and Freundlich isotherm model parameters for Methyl Orange, Coomassie Brilliant Blue, Congo Red and Eosin B uptake capacities on hierarchical flower-like CoAl-LDHs hollow microspheres

Sample name	**Langmuir**			**Freundlich**		
	q_m **(mg/g)**	b **(L mg^{-1})**	**R^2**	K_F **(L mg^{-1})**	**1/n**	**R^2**
CoAl-LDH-Methyl Orange	816.0	0.1776	0.9891	302.4	0.1772	0.9235
CoAl-LDH-Coomassie Brilliant Blue	654.8	0.05807	0.9849	152.9	0.2523	0.9595
CoAl-LDH-Congo Red	178.3	0.3050	0.9677	69.43	0.2158	0.9423
CoAl-LDH-Eosin B	95.14	2.411	0.9626	51.84	0.1469	0.9539

Table S2 Comparison of adsorption capacities for methyl orange on different adsorbents

Sample name	**Surface area/m^2/g**	**Qm/mg/g**	**T/K**	**Reference**
Co–Al–SO_4-LDH nanoscroll	63.49	1130	303	*J. Mater. Chem. A*, 2015, 3, 23395–23402
MnO_2–G–CNT	173.45	476.19 253.81	273 298	*New J. Chem.*, 2015, 39, 5484--5492
Mg−Al−LDH−NO_3		1800.3	298	*J. Phys. Chem. C*, 2015, 119, 23388−23397
CNT@MCo_2O_4(M = Ni, Mn, Cu, Zn)	144.0, 103.64, 73.45, 120.58	1188.3, 790.5, 826.9 , 935.4		*RSC Adv.*, 2015, 5, 79765–79773
calcined Zn/Al–CO_3–LDH		181.9	298	*J. Colloid Interf. Sci.*, 2007, 316, 284–291
rGO/Ni/MMO		210.8	298	*J. Colloid Interf. Sci.*, 2013, 408, 25–32
NH_2-MWCNTs	159.69	185.53	273	*RSC Adv.*, 2014, 4, 55162–55172
Mn_3O_4/KCC-1		746	273	*RSC Adv.*, 2015, 5, 106068–106076
H-d-MnO_2 nanosheets	166.07	357	293	*J. Mater. Chem. A*, 2015, 3, 5674–5682
H-d-MnO_2 nanoparticles	91.55	427		
CoAl-LDHs solid microspheres		770	298	this study
CoAl-LDHs hollow microspheres	167	816	298	this study

Table S3 The information of four anionic dyes

Dye name	Chemical formula	Structural formula	Width& Length*	Molecular weight/g/mol
Methyl Orange	$C_{14}H_{14}N_3SO_3Na$		**5.5 Å & 15 Å**	**327.33**
Coomassie Brilliant Blue	$C_{47}H_{48}N_3S_2O_7Na$		**21.6 Å & 21.8 Å**	**854.02**
Congo Red	$C_{32}H_{22}N_6S_2O_6Na_2$		**7.4 Å & 26.7 Å**	**696.66**
Eosin B	$C_{20}H_6Br_2N_2O_9Na_2$		**12.4 Å & 10.3 Å**	**624.06**

*: Calculated by GaussView 5.0