Supporting Information

Experimental and theoretical calculation investigation of 2,4-dichlorophenoxyacetic acid adsorption onto core-shell carbon microspheres@layered double hydroxides composites

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Supporting information includes 16 pages with 9 figures and 5 tables

Preparation of carbon microsphere (CMS) template

Briefly, 16 g of glucose and 2 g boric acid were dissolved in 40 mL of deionized water. Then, the solution was added to a 50 mL Teflon-lined autoclave and heated for 12 h at 180 ^{o}C. The resultant solution was sequentially washed with deionized water and dried at 60 ^{o}C overnight, yielding the powder of CMS.

Preparation of LDHs.

A mixing metal chloride aqueous solution of $M^{2+}Cl_2$ and $AlCl_3 \cdot 6H_2O$ was prepared with a 3:1 M^{2+}/Al^{3+} molar ratio (total cation concentration of 0.5 M, $M^{2+} = Mg^{2+}$, Zn^{2+}, Ni^{2+}, respectively). Diluted ammonia (5:1, v/v) was then slowly added into the mixing solution. The product was then filtered and washed with distilled water. The MgAl-LDHs were aged at 80^{o}C for 6 h in an oven to convert into LDHs sol. The NiAl-LDHs and ZnAl-LDHs were mixed with deionized water and vigorous stirring to convert into gel.

Directly assembly of LDHs on the surface of CMS.

The LDHs sol precursor (LDHs solid content of 1 g) was dispersed into 25 mL of methanol by ultrasonication for 15 min to obtain a stable colloidal solution. The CMS powder (500 mg) was ultrasonically mixed with 50 mL of methanol for 15 min to produce a suspension of CMS. This suspension was then mixed with the LDHs colloidal solution and was ultrasonicated at room temperature for 30 min. Afterwards, the CMS@LDHs composite particles were centrifuged and dried at 60 ^{o}C for 12 h.

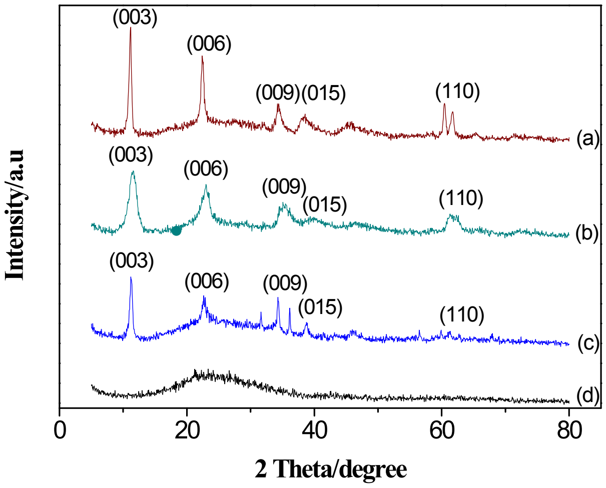


Fig. S1 XRD pattern of MgAl-LDHs (a), NiAl-LDHs (b), ZnAl-LDHs (c) and CMS (d).

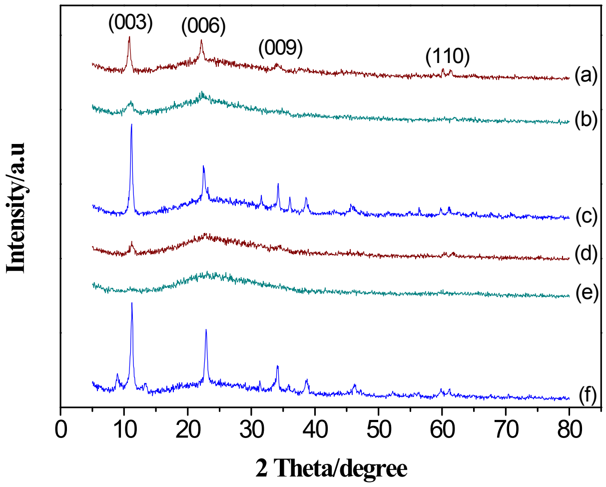


Fig. S2 XRD pattern of CMS@MgAl-LDHs (a), CMS@NiAl-LDHs (b) and CMS@ZnAl-LDHs (c) before adsorbing 2,4-D and CMS@MgAl-LDHs (e), CMS@NiAl-LDHs (f) and CMS@ZnAl-LDHs (g) after adsorbing 2,4-D.

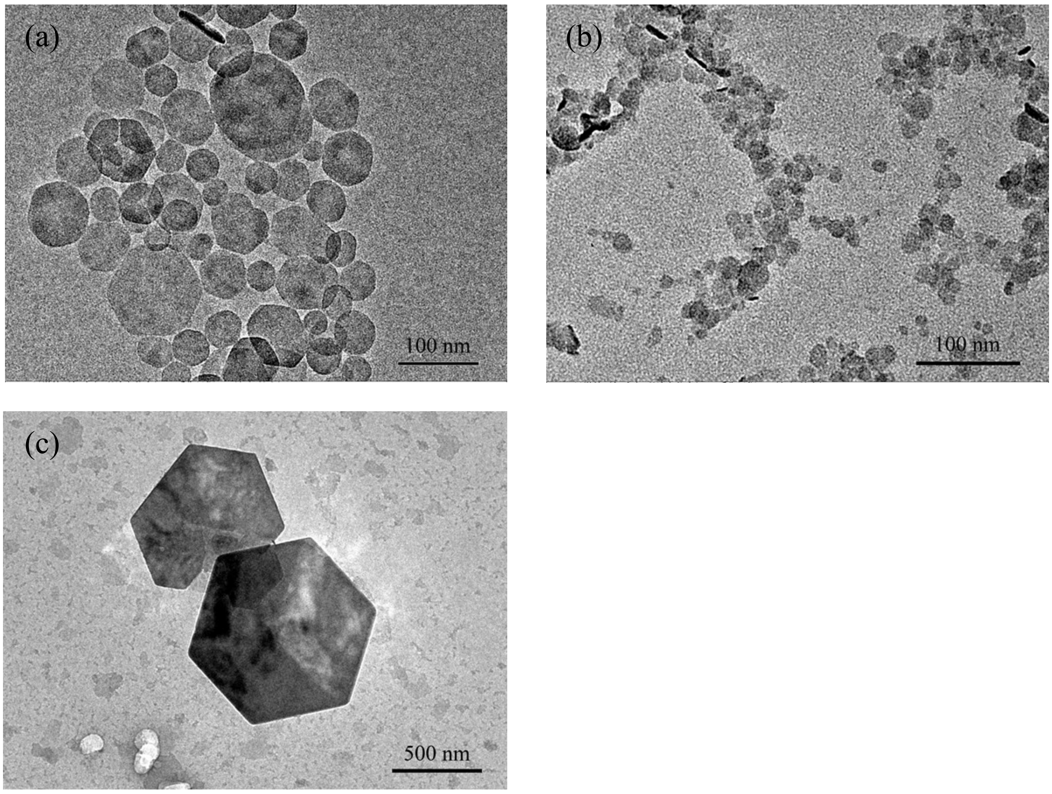


Fig. S3 TEM images of MgAl-LDHs (a), NiAl-LDHs (b) and ZnAl-LDHs (c).

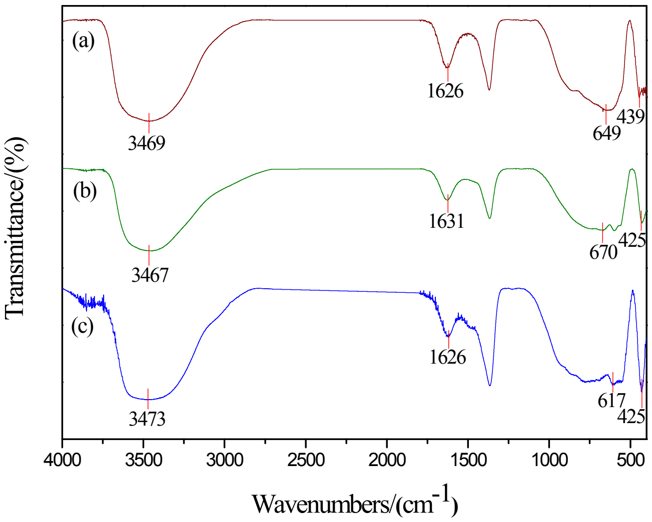


Fig. S4 FTIR spectra of MgAl-LDHs (a), NiAl-LDHs (b) and ZnAl-LDHs (c).

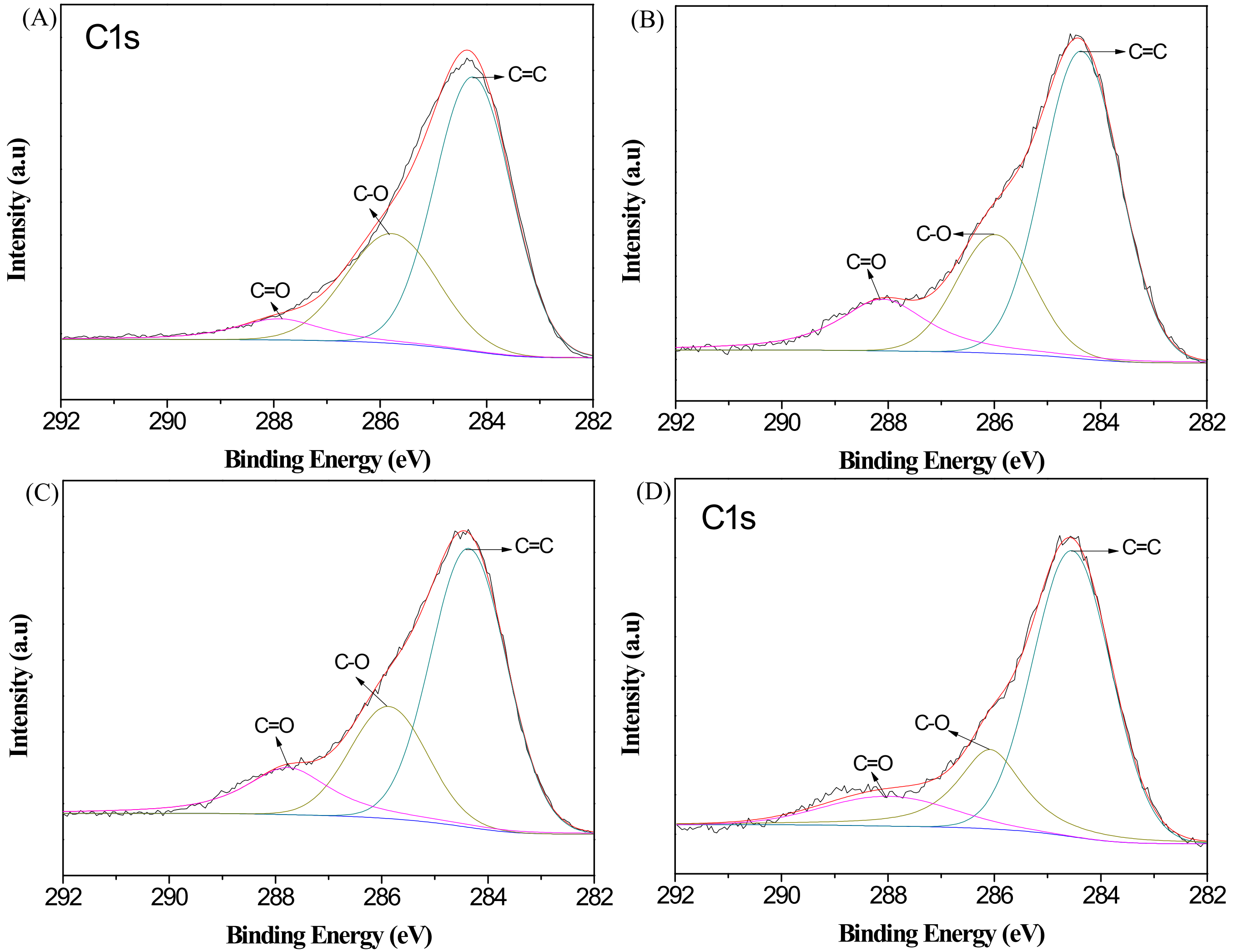


Fig. S5 HR-XPS spectra of C1s for CMS (A), CMS@MgAl-LDHs (B), CMS@NiAl-LDHs (C), and CMS@ZnAl-LDHs (D) before adsorbing 2,4-D.

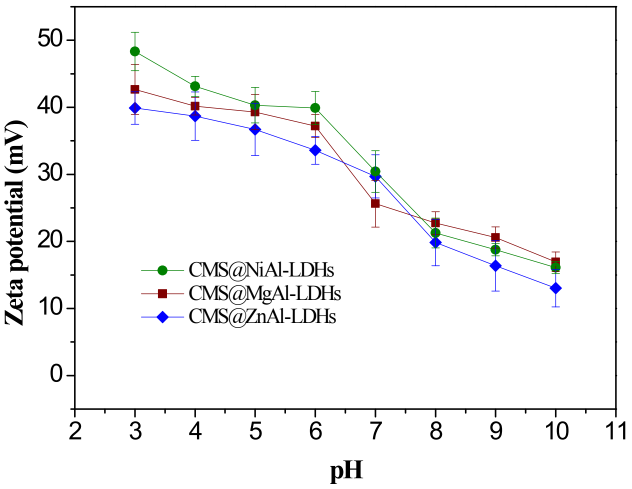


Fig. S6 The relationship of zeta potential of CMS@LDHs and solution pH.

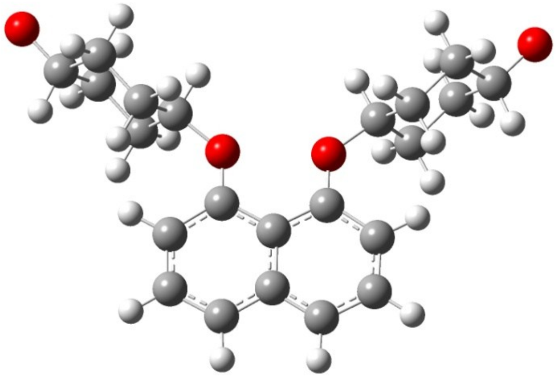
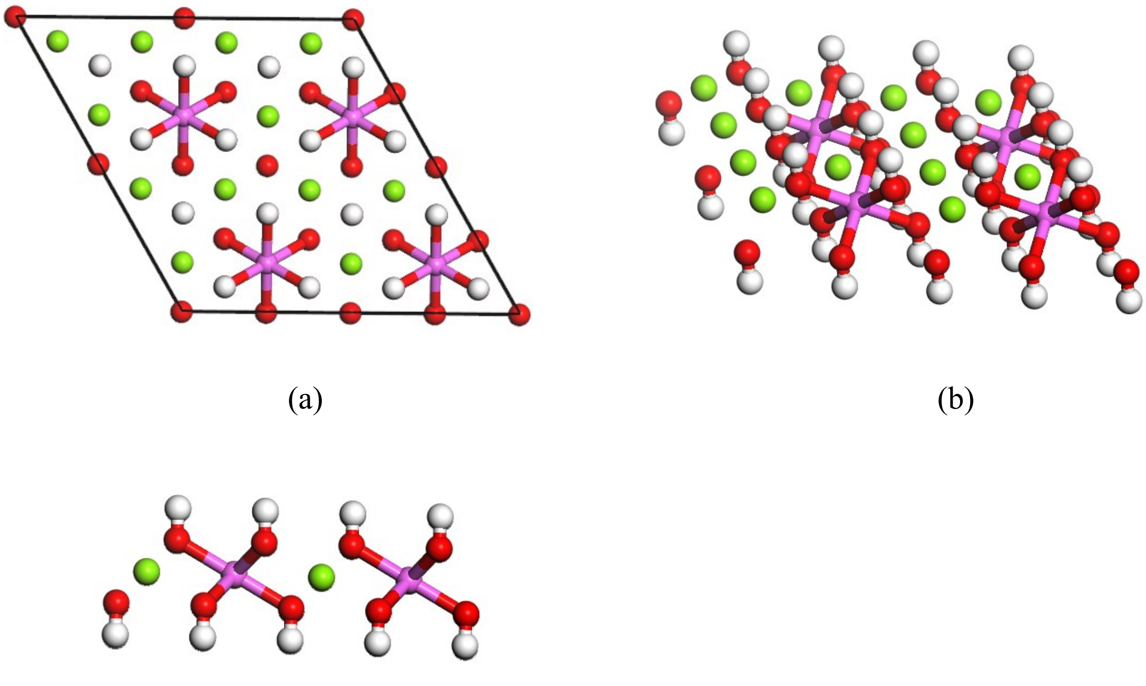


Fig. S7 Optimized geometrical structure of the CMS with carbonized core and polysaccharides surfaces. Red atoms are oxygen, white atoms are hydrogen, dark green atoms are chlorine, gray atoms are carbon.

Density Functional Theory Calculations

Layered double hydroxides whose microstructure with a Mg^{2+}/Al^{3+} ratio of three were constructed in this study. The atomic position was obtained from the crystal structure with the space group of rhombohedral (R-3m) and unit cell parameters of $a = b = 12.184$ Å, $c = 18$ Å; $\alpha = \beta = 90$, $\gamma = 120$. The vacuum gap along the normal to the surface was 15 Å. The 4×4×1 supercell of the simulated hydroxide layer was shown in Fig. S8.

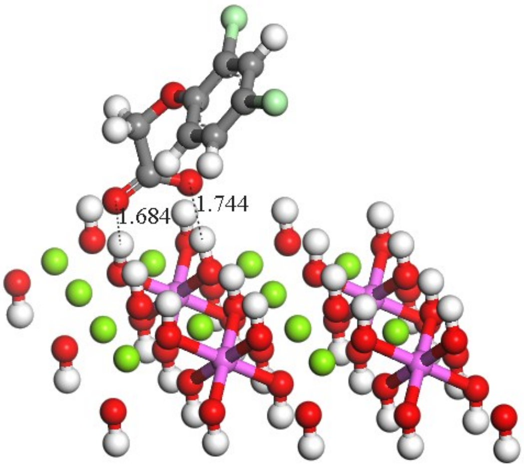


(a)

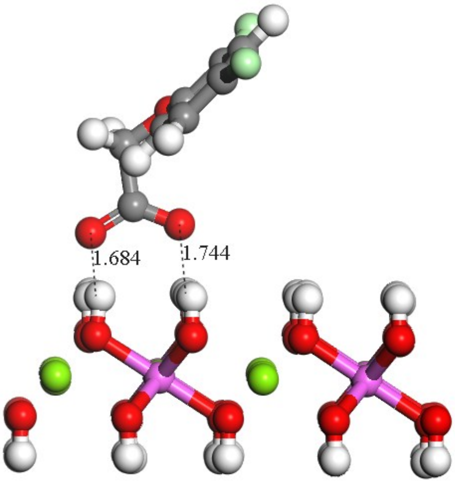
(b)

(c)

Fig. S8 Top view (a) and side view (b,c) of the Mg/Al-LDHs model with a Mg/Al ratio of three. Red atoms are oxygen, white atoms are hydrogen, light green atoms are aluminum, and pink atoms are magnesium.



(a)



(b)

Fig. S9 Optimized geometrical structure of 2,4-dichlorophenoxyacetic acid adsorbed onto LDHs nanosheets depicting the side view (a,b). Red atoms are oxygen, white atoms are hydrogen, dark green atoms are chlorine, light green atoms are aluminum, and pink atoms are magnesium.

Table S1 Summary of BET surface, Zeta potential and Average particle diameter analysis of CMS and CMS@LDHs composites.

Sample	BET surface (m^2/g)	Zeta potential (mV)
CMS	16.36	-24.21
CMS@MgAl-LDHs	50.32	+39.28
CMS@NiAl-LDHs	46.36	+43.19
CMS@ZnAl-LDHs	44.24	+35.77

Table S2 Peak parameter and relative contents of different groups of CMS and CMS@LDHs composites.

Types of LDHs	Relative contents of different group (%)			E_B (eV)		
	C=C	C=O	C-O	C=C	C=O	C-O
CMS	81.34	8.79	9.86	284.6	287.9	286.2
CMS-MgAl-LDH	60.49	16.39	23.12	284.3	288.0	285.9
CMS-NiAl-LDH	59.84	15.79	24.36	284.4	287.8	285.9
CMS-ZnAl-LDH	66.98	11.49	21.52	284.5	287.9	286.0

Table S3 Relative contents of different groups of CMS@LDH composites before and after adsorbing 2,4-D obtained from XPS analysis (C 1s spectrum).

Types of LDHs	Relative contents of different group (%)			
	C=C	C=O	C−O	O−C=O
CMS@MgAl-LDH	60.49	16.39	23.12	—
CMS@MgAl-LDH+2,4-D	56.39	8.18	31.73	3.69
CMS@NiAl-LDH	59.84	15.79	24.36	—
CMS@NiAl-LDH+2,4-D	52.96	8.43	36.63	1.97
CMS@ZnAl-LDH	66.98	11.49	21.52	—
CMS@ZnAl-LDH+2,4-D	54.57	9.92	29.56	6.24

Table S4 Comparison of different adsorbents for 2,4-D removal from aqueous solution.

Adsorbents	2,4-D concentration (mg/L)	adsorbent dosage (g/L)	Adsorption equilibrium time (h)	Reference
Calained MgAl-LDHs	221	1.5	24	[1]
Calained MgAl-LDHs	265	4	6	[2]
Calcined Zn-Al-Zr-LDHs	100	5	1	[3]
Zn-Al-LDHs	221	1	12	[4]
MgAl-LDHs	200	1	6	This work
NiAl-LDHs	200	1	6	This work
CMS@MgAlLDHs	200	1	1	This work
CMS@NiAlLDHs	200	1	1.2	This work
CMS@ZnAlLDHs	200	1	1.6	This work

[1] Pavlovic, I.; Barriga, C.; Hermosin, M. C.; Cornejo, J.; Ulibarri, M. A., Adsorption of acidic pesticides 2, 4-D, Clopyralid and Picloram on calcined hydrotalcite. *Appl. Clay Sci.* **2005,** *30* (2), 125-133.

[2]Cardoso, L. P.; Valim, J. B., Study of acids herbicides removal by calcined Mg—Al—CO_3—LDH. *J. Phys. Chem. Solids* **2006,** *67* (5–6), 987-993.

[3] Chaparadza, A.; Hossenlopp, J. M., Removal of 2, 4-dichlorophenoxyacetic acid by calcined Zn–Al–Zr layered double hydroxide. *J. Colloid Interface Sci.* **2011,** *363* (1), 92-97.

[4] Legrouri, A.; Lakraimi, M.; Barroug, A.; De Roy, A.; Besse, J. P., Removal of the herbicide 2,4-dichlorophenoxyacetate from water to zinc–aluminium–chloride layered double hydroxides. *Water Res.* **2005,** *39* (15), 3441-3448

Table S5 Thermodynamic parameters for adsorption of 2,4-D onto CMS@LDHs composites.

Samples	Temperature (K)	ΔG^o (KJ/mol)	ΔH^o (KJ/mol)	ΔS^o (J/mol K)
CMS@MgAl-LDHs	298	-9.79	25.23	117.56
	308	-10.99		
	318	-12.15		
CMS@NiAl-LDHs	298	-9.24	24.89	114.40
	308	-10.23		
	318	-11.54		
CMS@ZnAl-LDHs	298	-8.64	20.30	97.05
	308	-9.55		
	318	-10.59		