Supporting Information

for

Electro Assisted Selective Uptake / Release of Phosphate using Graphene Oxide/MgMn-Layered Double Hydroxide Composite

Yi-Ting Lai,^a Wei-Ting Liu,^a Lih-Juann Chen,^a Min-Chao Chang,^b Chi-Young Lee,^a

and Nyan-Hwa Tai*a

^{a.} Department of Materials Science and Engineering, National Tsing-Hua University, No. 101, Sec. 2,

Kuang-Fu Rd., Hsin-chu, 30013, Taiwan

^{b.} Material and Chemical Research Laboratories, Industrial Technology Research Institute (ITRI),

Bldg. 17, 321 Sec. 2, Kuang-Fu Road, Hsinchu, 30011, Taiwan

*Corresponding author at: Department of Materials Science and Engineering, National Tsing-Hua University

Address: No. 101, Sec. 2 Kuang-Fu Rd. Hsin-chu, 30013 Taiwan

Tel: +886 35715131#42568

Fax: + 886 3 5737406

E-mail: <u>nhtai@mx.nthu.edu.tw</u> (Nyan-Hwa Tai); <u>laieating@yahoo.com.tw</u> (Yi-Ting Lai); <u>cylee@mx.nthu.edu.tw</u> (Chi-Young Lee); <u>s101031904@m101.nthu.edu.tw</u> (Wei-Ting Liu); <u>ljchen@mx.nthu.edu.tw</u> (Lih-Juann Chen); <u>minchaochang@itri.org.tw</u> (Min-Chao Chang)

1. Fabrication of electrodes

Two kinds of LDH slurries were prepared by individually mixing the MgMn-LDH-300 and GO/MgMn-LDH-300 composites (70 wt.%) with graphite (3.5 μ m, Emaxwin Technology Co., Ltd.; 20 wt.%) and polyvinylidene fluoride (PVDF, M.W. 514,000, Aldrich; 10 wt.%), which were then dissolved in N-methyl-2-pyrrolidone (NMP, Aldrich) and mixed subsequently for 2 h. The homogenous LDH slurries were separately cast onto titanium foil, used as a current collector (300 μ m wet thickness), using the doctor blade technique. The coated LDH electrode was then dried at 140°C in an oven for 4 h to remove the organic solvents.

Carbon electrodes were fabricated utilizing a carbon slurry containing activated carbon powder (petroleum coke, Formosa Plastics Corporation, Taiwan; 80 wt.%), PVDF (10 wt.%), and graphite (10 wt.%) dissolved in NMP. The processing used for the preparation of carbon electrodes was the same as that for the LDH electrodes.

2. Electrochemical characterization of the electrodes

Electrochemical analysis was conducted using a CHI 614D workstation (CH Instruments, Austin, TX). Cyclic voltammetry (CV) and linear sweep voltammetry (LSV) curves were derived from the use of a three-electrode cell with a Pt wire and an Ag/AgCl electrode as the counter and the reference electrodes, respectively. The size of the working electrode was 1 cm \times 1 cm, the potential range was from 0.0 to 1.0 V, the specific scan rate was 10 mV/s, and a Na₂HPO₄ solution with a concentration of 100 mg/L was used as the electrolyte.

3. Morphology characterizations of LDH composites

The morphologies of MgMn-LDH, GO/MgMn-LDH and their calcined samples were examined through FESEM and high resolution TEM shown in **Figure S1**. All the LDH composites are observed in a sheet-like particles. FESEM images of GO/MgMn-LDH and GO/MgMn-LDH-300 shown in

Figure S1c and S1d, respectively, depict smaller particle sizes than MgMn-LDH and MgMn-LDH-300, as shown Figure S1a and S1b, respectively. This result illustrated that the introduction of GO resulted in a looser crystallinity of LDH composites, which reduces the particle sizes. In addition, small particle size increased surface area of LDH composites, and subsequently enhanced the phosphate removal performance[1]. As shown in Figure S1e, stacked layers with folds form 3D structure of GO/MgMn-LDH, which was beneficial for ion diffusion during the electrosorption process[2]. TEM image, as shown in Figure S1f, indicates that GO/MgMn-LDH are layered structure. The images demonstrated that GO and MgMn-LDH were well incorporated to form the synergetic composite materials.



Figure S 1. FESEM images of (a) MgMn-LDH, (b) MgMn-LDH-300, (c) GO/MgMn-LDH, and (d) GO/MgMn-LDH-300 composites. (e) enlarged FESEM image for 3D structure of GO/MgMn-LDH composites. (f) TEM image of GO/MgMn-LDH composites.

4. The phosphate adsorption capacity and kinetics of LDH composites

The pseudo-first-order and pseudo-second-order equations were used to study the adsorption kinetics of phosphate and were listed in equations (1) and (2)[3], respectively,

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303}t$$
(1)
$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$
(2)

where q_e (mg/g) is the phosphate adsorption capacity at equilibrium, q_t (mg/g) is the phosphate adsorption capacity at time t (min). k_1 (1/min) and k_2 (g/(mg-P min)) are the rate constant of pseudofirst-order and pseudo-second-order models, respectively. Parameters of both kinetic model were analyzed by fitting the experimental data, and the results are depicted in **Figure S2** and summarized in **Table 1**. The results show that pseudo-second-order model is appropriate to describe the phosphate adsorption kinetics for both adsorbents with higher correlation coefficients (R^2). It suggests that the phosphate adsorption process is dominated by chemisorption between phosphate and active sites on LDH composites.



Figure S 2. (a) The pseudo-first-order kinetic and (b) pseudo-second-order kinetic curves fitting for phosphate adsorption by MgMn-LDH-300 and GO/MgMn-LDH-300 electrodes.

5. Comparison of phosphate adsorption and desorption efficiencies of this work with other published studies.

Table S1. Comparison of phosphate adsorption efficiency of this work with previous studies

Adsorbent	рН	Initial HPO4 ²⁻ concentration (ppm)	Solution volume (mL)	Adsorption capacity (mg-P/g)	Adsorption rate (mg- P/g/min)	Ref.
MgMn-LDH-300	8.0	384	50	34.1	0.01	[1, 2]
BR-LDH	7.0	100	50	18.6	0.09	[4]
RGO-Zr	5.0	10	200	27.7	0.02	[5]
Mg/Al-LDH	9.0	9600	200	57.3	0.08	[6]
Mg/Al-LDHs biochar	3.0	50	20	81.8	0.06	[7]
MgFe–Zr-LDH	7-8	10	100	30.0	0.02	[8]
Lanthanum hydroxides	N.A.	200	40	107.5	0.07	[9]
Zn ₂ Al-PMA-LDH	3.0	100	N.A.	76.0	0.32	[10]
MgMn-LDH-300	6.7	100	200	26.0	0.43	Our work
GO/MgMn-LDH- 300	6.7	100	200	70.8	0.79	Our work

Adsorbent	Regeneration solution	Solution volume (mL)	Temp (℃)	Desorption capacity (mg-P/g)	Desorption rate (mg- P/g/min)	Ref
MgMn-LDH-300	5 M NaCl + 0.1 M NaOH	2000	25	23.8	0.02	[1, 2]
BR-LDH	0.1 M Na ₂ CO ₃	N.A.	N.A.	16.7	N.A.	[4]
RGO-Zr	N.A.	N.A.	N.A.	N.A.	N.A.	[5]
Mg/Al-LDH	0.003 M DBS	150	25	52.1	0.02	[6]
Mg/Al-LDHs biochar	рН 10.91	20	23	28.0	0.02	[7]
MgFe–Zr LDH	0.1 M NaOH + 2.0 M NaCl	100	N.A.	30.0	0.02	[8]
Lanthanum hydroxides	3 M NaOH	40	250	63.2	0.21	[9]
Zn ₂ Al-PMA-LDH	0.1M NaOH	N.A.	30	31.2	0.13	[10]
GO/MgMn-LDH- 300	0.01 M NaCl + NaOH	200	25	35.6	3.56	Our work

Table S2. Comparison of phosphate desorption efficiency of this work with previous studies.

6. Selectivity of phosphate adsorption-desorption characterizations of LDH samples

The selective phosphate adsorptions by MgMn-LDH-300 and GO/MgMn-LDH-300 were assessed in a solution with the presence of sulfate as a competing anion at the same concentration as the phosphate. Their uptake and distribution coefficients (K_d) are summarized in **Table S3**. K_d was calculated using the following equation[11]:

 K_d (cm³/g) = Ion adsorption capacity (mg/g)/Final ion concentration (mg/cm³). (1)

The phosphate selectively coefficient is defined as the K_d of phosphate divided by the K_d of the competing ion. The phosphate-to-sulfate selectively coefficients were 7.7 and 52.0 for MgMn-LDH-300 and GO/MgMn-LDH-300, respectively. This indicates that phosphate selectivity is improved

owing to the introduction of GO. This is especially advantageous for the removal of phosphate from wastewater or seawater, both of which usually contain a large amount of SO_4^{2-} ions[11].

Adsorbent	HPO4 ²⁻ uptake (mg/g)	<i>K</i> _d of HPO ₄ ²⁻ (cm ³ /g)	SO4 ²⁻ uptake (mg/g)	<i>K</i> _d of SO ₄ ²⁻ (cm ³ /g)	Selectively coefficient (K _d -P/ K _d -S)
MgMn-LDH-300	2.9	831	0.9	108	7.7
GO/MgMn-LDH-300	8.0	2701	0.7	52	52.0

Table S3. Ions uptakes and distribution coefficients by MgMn-LDH-300 and GO/MgMn-LDH-300.

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