Supporting Information

for

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

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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 μm, 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 μm 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 × 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,

$$\log (q_e - q_t) = \log q_e - \frac{k_1}{2.303} t$$  \hspace{2cm} (1)

$$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$$  \hspace{2cm} (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 pseudo-first-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.

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>pH</th>
<th>Initial HPO$_4^{2-}$ concentration (ppm)</th>
<th>Solution volume (mL)</th>
<th>Adsorption capacity (mg-P/g)</th>
<th>Adsorption rate (mg-P/g/min)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgMn-LDH-300</td>
<td>8.0</td>
<td>384</td>
<td>50</td>
<td>34.1</td>
<td>0.01</td>
<td>[1, 2]</td>
</tr>
<tr>
<td>BR-LDH</td>
<td>7.0</td>
<td>100</td>
<td>50</td>
<td>18.6</td>
<td>0.09</td>
<td>[4]</td>
</tr>
<tr>
<td>RGO-Zr</td>
<td>5.0</td>
<td>10</td>
<td>200</td>
<td>27.7</td>
<td>0.02</td>
<td>[5]</td>
</tr>
<tr>
<td>Mg/Al-LDH</td>
<td>9.0</td>
<td>9600</td>
<td>200</td>
<td>57.3</td>
<td>0.08</td>
<td>[6]</td>
</tr>
<tr>
<td>Mg/Al-LDHs biochar</td>
<td>3.0</td>
<td>50</td>
<td>20</td>
<td>81.8</td>
<td>0.06</td>
<td>[7]</td>
</tr>
<tr>
<td>MgFe–Zr-LDH</td>
<td>7-8</td>
<td>10</td>
<td>100</td>
<td>30.0</td>
<td>0.02</td>
<td>[8]</td>
</tr>
<tr>
<td>Lanthanum hydroxides</td>
<td>N.A.</td>
<td>200</td>
<td>40</td>
<td>107.5</td>
<td>0.07</td>
<td>[9]</td>
</tr>
<tr>
<td>Zn$_2$Al-PMA-LDH</td>
<td>3.0</td>
<td>100</td>
<td>N.A.</td>
<td>76.0</td>
<td>0.32</td>
<td>[10]</td>
</tr>
<tr>
<td>MgMn-LDH-300</td>
<td>6.7</td>
<td>100</td>
<td>200</td>
<td>26.0</td>
<td><strong>0.43</strong></td>
<td><strong>Our work</strong></td>
</tr>
<tr>
<td>GO/MgMn-LDH-300</td>
<td>6.7</td>
<td>100</td>
<td>200</td>
<td>70.8</td>
<td><strong>0.79</strong></td>
<td><strong>Our work</strong></td>
</tr>
</tbody>
</table>
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]:

$$K_d \text{ (cm}^3\text{/g)} = \frac{\text{Ion adsorption capacity (mg/g)}}{\text{Final ion concentration (mg/cm}^3\text{)}}.$$

(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 $\text{SO}_4^{2-}$ ions[11].

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

<table>
<thead>
<tr>
<th>Adsorbent</th>
<th>$\text{HPO}_4^{2-}$ uptake (mg/g)</th>
<th>$K_d$ of $\text{HPO}_4^{2-}$ (cm$^3$/g)</th>
<th>$\text{SO}_4^{2-}$ uptake (mg/g)</th>
<th>$K_d$ of $\text{SO}_4^{2-}$ (cm$^3$/g)</th>
<th>Selectively coefficient ($K_d$ -P/$K_d$ -S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgMn-LDH-300</td>
<td>2.9</td>
<td>831</td>
<td>0.9</td>
<td>108</td>
<td>7.7</td>
</tr>
<tr>
<td>GO/MgMn-LDH-300</td>
<td>8.0</td>
<td>2701</td>
<td>0.7</td>
<td>52</td>
<td>52.0</td>
</tr>
</tbody>
</table>

### References


