Supporting Information

Mussel-Inspired Synthesis of Polydopamine-Functionalized Calcium Carbonate as Reusable Adsorbents for Heavy Metal Ions

Chengyong Li,*[abc] Zhong-ji Qian,[d] Chunxia Zhou,[ab] Weiming Su,[b] Pengzhi Hong,[ab] Shucheng Liu,[ab] Lei He,[a] Zhimeng Chen[a] and Hongwu Ji*[abc]

[a] *College of Food Science and Technology, Guangdong Ocean University, Zhanjiang 524088, China.*
[b] *Guangdong Provincial Key Laboratory of Aquatic Product Processing and Safety, Guangdong Ocean University, Zhanjiang 524088, China.*
[c] *Key Laboratory of Advanced Processing of Aquatic Products of Guangdong Higher Education Institution, Guangdong Ocean University, Zhanjiang 524088, China.*
[d] *Department of Chemistry, Pukyong National University, Busan 608737, Korea*
Tel: +86-759-2396270; Fax: +86-759-2396270
E-mail: cyli@gdou.edu.cn, jihw62318@163.com

Table of Contents

1. Reagents

Waste shells of ostracean were collected from the local markets and were washed, sun dried. Dopamine was purchased from Sigma-Aldrich. All other reagents were of analytical grade. All solutions were prepared using ultrapure water (18.3MΩ·cm) from the Millipore Milli-Q system.

2. Preparation of samples

Waste shells of ostracean were calcined in the atmosphere at different temperatures to remove the organics. Using simple thermal calcination in air, the chitin and protein organic components in the shells can be removed to form pure $CaCO_3$. Then pure $CaCO_3$ powers were dipped into the 5 mM dopamine buffer solution (Tris-HCl, pH=8.5). After deposition for 6 h, $CaCO_3$ powers modified with dopamine (PDA- $CaCO_3$) were rinsed by deionized water and freezed drying.

3. Materials characterization

Scanning electron microscopy (SEM) images were acquired on a Scanning Electron Microscope (S-4800 Hitachi, Japan) with a 8~10 mm working distance and 10 kV accelerating voltage. Specific surface of the samples were measured on Specific Surface Tester (ASAP 2020, Micromeritics Instrument, America). Infrared transmission spectra of the samples were performed on Fourier Transform Infrared Spectrometer (Nicolet 6700, Thermo Fisher Scientific, America). X-ray photoelectron spectroscopy (XPS) of the samples were measured using a X-ray Photoelectron Spectroscopy (Al K-Alpha, Thermo Fisher Scientific, America). Sample chamber pressure was 5×10^{-9} torr. X-ray power was 72 W and the diameter was 50 μm. Zeta potential of was measured using Zeta Potential Analyzer (Zetasizer Nano, Malvern, UK). The concentration of metal ions was determined by Graphite Furnace Atomic Absorption Spectrometer (Thermo M, Thermo Fisher Scientific, America).

4. Adsorption equilibrium experiments

Batch adsorption experiments were carried out at room temperature to investigate the adsorption behaviors of Pb(II) and Cd(II). Typically, 10 mg PDA-$CaCO_3$ or pure

$CaCO_3$ was placed into 100 mL aqueous solutions containing one of the pollutants with different concentrations in a flask and was shaken in a thermostatic reciprocating shaker for 24 h to reach adsorption equilibrium. After adsorption, the free-standing PDA-$CaCO_3$ or pure $CaCO_3$ was directly removed from the solution by centrifugal separation (1000 r/min, 5 min). The concentrations of the heavy metals ions remaining in the solution were measured by atomic absorption spectroscopy. The amount of the heavy metal ions at equilibrium q_e (mg/g) on the adsorbent samples were calculated according the following equation:

$$q_e = (C_0 - C_e)V / W \tag{1}$$

Where C_0 and C_e represent the initial and equilibrium concentrations (mg g^{-1}), respectively, where V is the volume of the solutions (mL), and W is the amount of the adsorbents (mg).

The adsorption capacities of the two adsorbents progressively increased with increasing concentrations of metals ions, and finally reached the saturation states (Figure 6). These adsorption data were fitted into the Langmuir isotherm models (2) with the equations given as following:

$$q_e = q_{\max} K_L C_e / (1 + K_L C_e) \tag{2}$$

Where q_e is the amount (mg g^{-1}) of metal ions adsorbed at equilibrium, C_e is the equilibrium concentration (mg L^{-1}) of metal ions, K_L and q_{max} (maximum adsorption capacity) are the Langmuir constants of adsorption.

In order to study the influence of pH on the removal efficiency, HCl solution was used to adjust and control the pH of the initial heavy metals solution. HCl solution (100 mL, 1 mM) was used as desorption agent for Pd(II) and Cd(II) to regenerate the adsorbents of PDA-$CaCO_3$ or pure $CaCO_3$ after shaken for 2 h.

5. Adsorption kinetic experiments

The adsorption kinetic experiments were identical to those of isotherm experiments. The aqueous samples were taken to preset time intervals and the concentrations of heavy metal ions were similarly measured. The amount of adsorption at time t, q_t (mg/g), was calculated by:

$$q_t = (C_0 - C_t)V/W \tag{3}$$

Where C_0 and C_t (mg/L) are the liquid phase concentrations of heavy metal ions at initial and any time t, respectively, where V is the volume of the solutions (mL), and W is the amount of the adsorbents (mg).

The pseudofirst order (3) and pseudosecond order (4) kinetic models were employed to fit the experimental data according to the equations as following:

$$\ln(q_e - q_t) = \ln q_e - k_1 t \tag{4}$$

$$t/q_t = 1/k_2\, q_e^2 + t/q_e \tag{5}$$

Where q_e and q_t are the capacities (mg g^{-1}) of metal ions adsorbed at equilibrium and time t (min), k_1 is the rate constant of pseudofirst order model (min^{-1}), and k_2 is the rate constant of the pseudosecond order model of adsorption (g mg^{-1} min^{-1}).

6. Fig. S1, Fig. S2, Fig. S3, Fig. S4, Fig. S5, Fig. S6

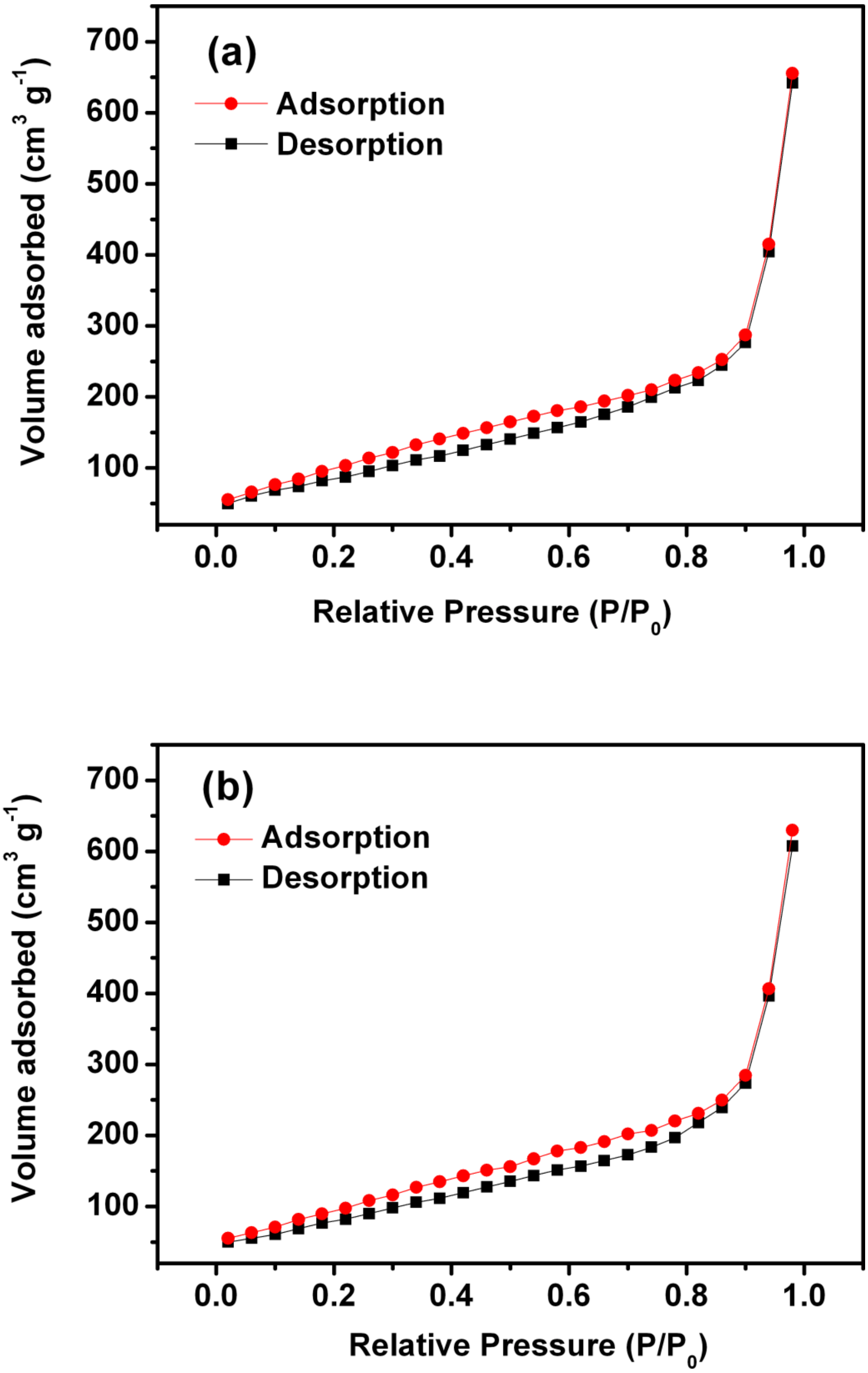

Fig.S1 Nitrogen gas adsorption and desorption isotherms of pure $CaCO_3$(a) and PDA-$CaCO_3$(b).

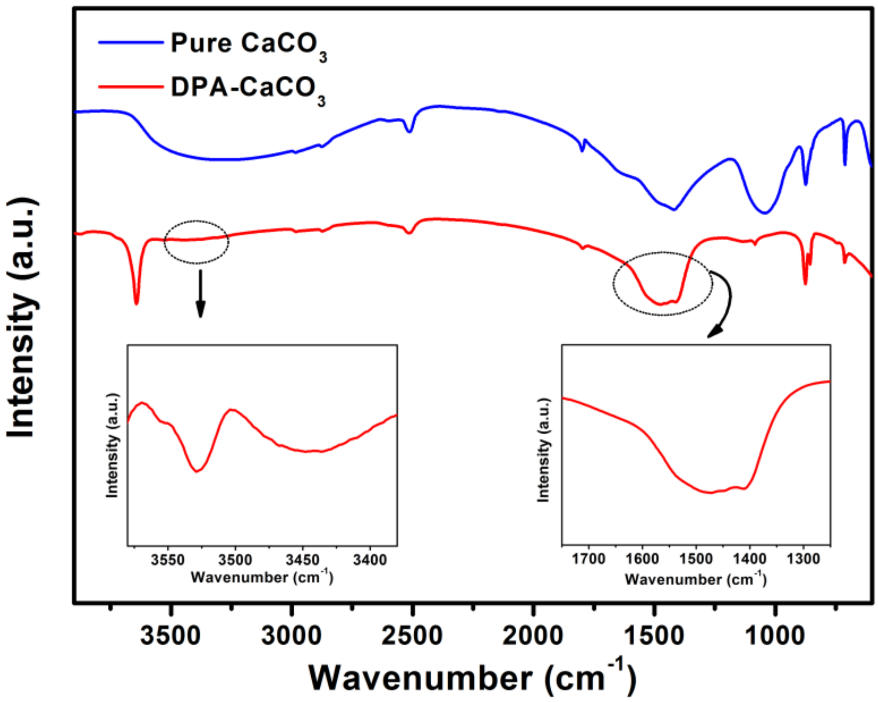

Fig.S2 IR of pure $CaCO_3$ and PDA- $CaCO_3$.

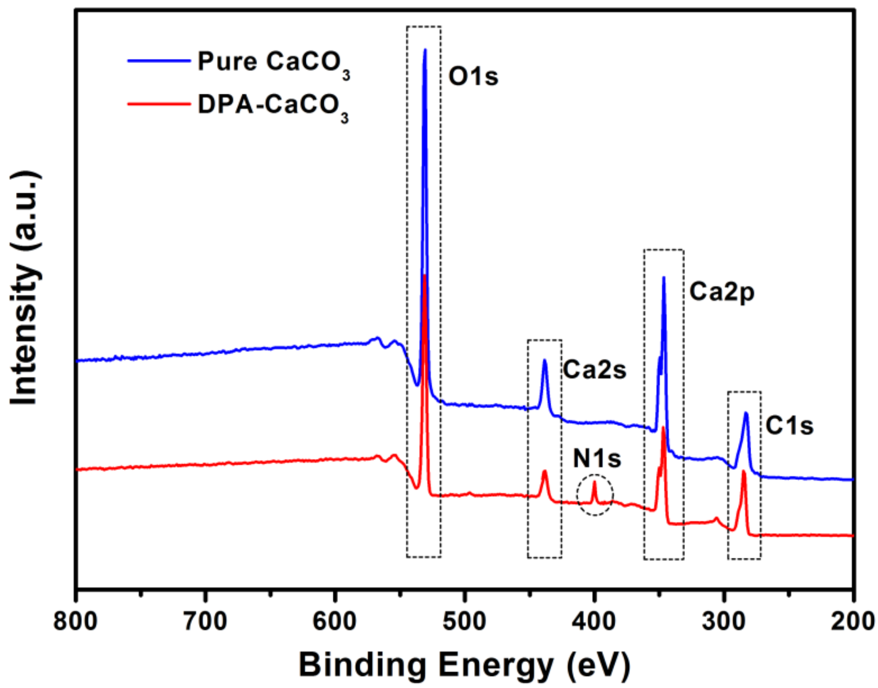

Fig.S3 XPS spectra of pure $CaCO_3$ and PDA- $CaCO_3$.

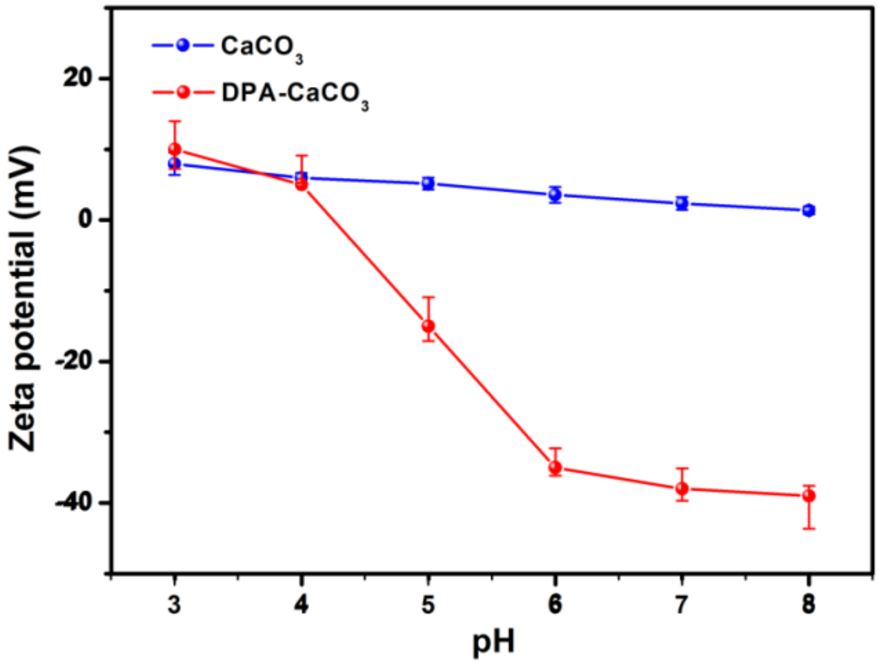

Fig.S4 Zeta-potentials of pure $CaCO_3$ and PDA- $CaCO_3$ under different pH values.

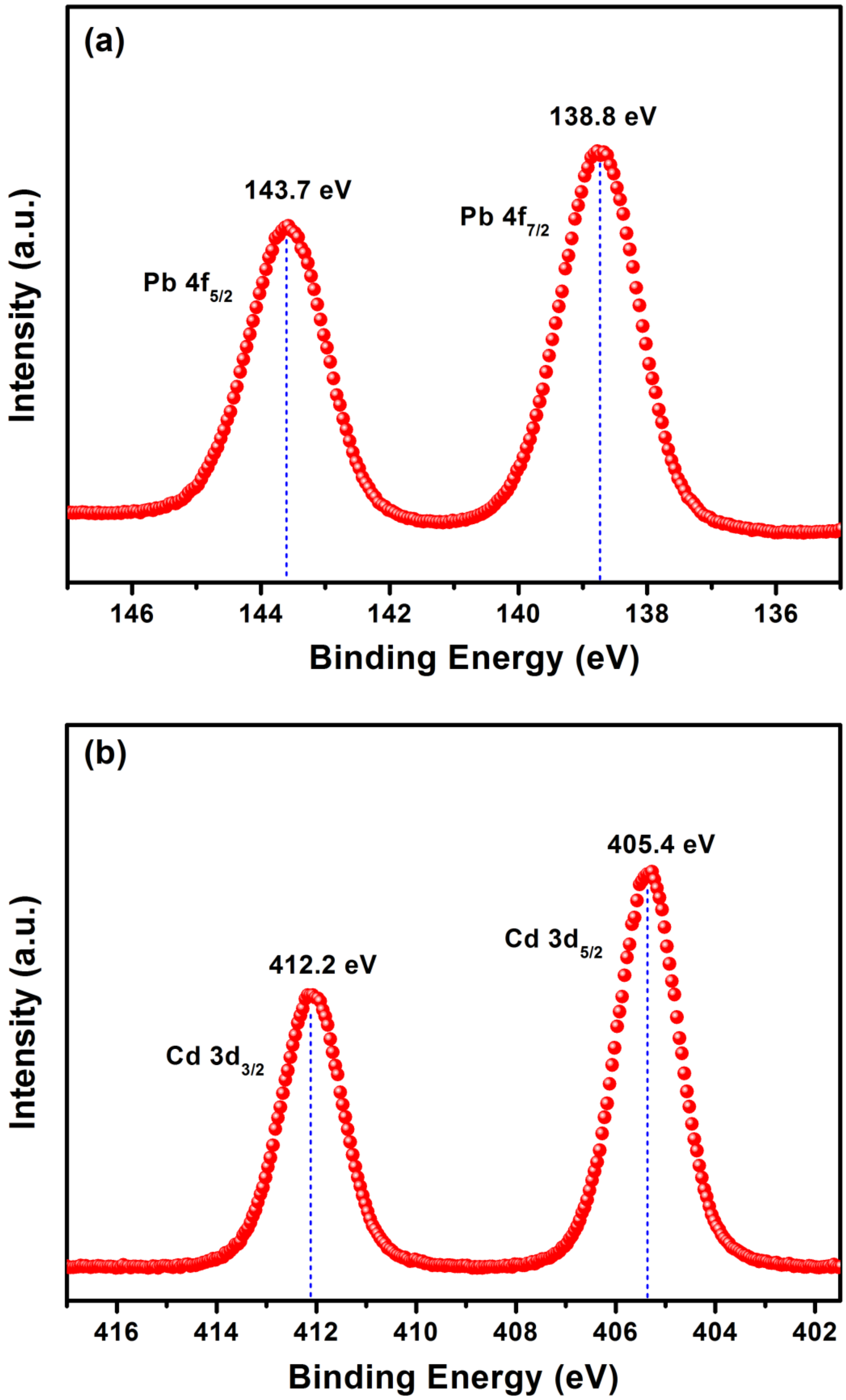

Fig.S5 XPS spectra of Pb 4f(a) and Cd 3d(b) after their adsorption on PDA- $CaCO_3$.

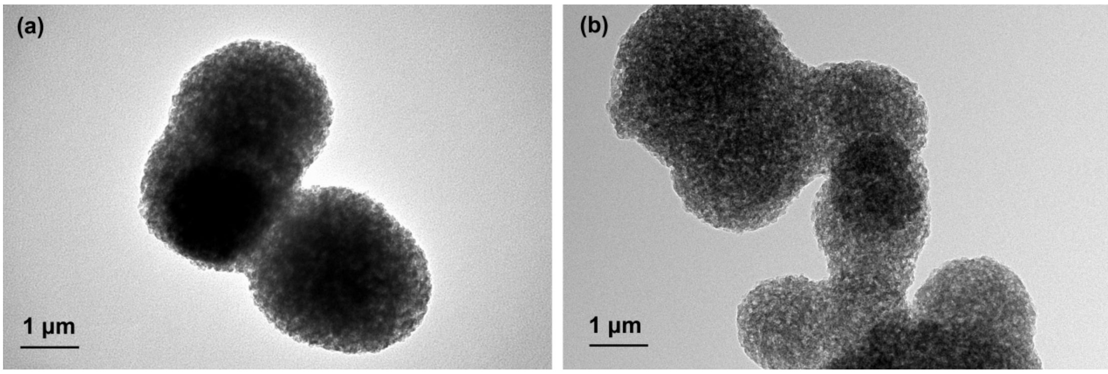

Fig.S6 TEM images of PDA- $CaCO_3$ after adsorption-desorption for the first time (a) and for the tenth time (b).

7. TableS1

Table S1 Comparison of the maximum adsorption capacities of various adsorbents for the heavy metal ions of Pb(II) and Cd(II).

Absorbents	Metal Ions	Pseudo-First Order model			Pseudo-Second Order model		
		r^2	q_e (mg g^{-1})	k_1 (min^{-1})	r^2	q_e (mg g^{-1})	k_1 (min^{-1})
PDA-$CaCO_3$	Pb(II)	0.9577	265.43	0.058	0.9960	282.65	0.41×10^{-3}
PDA-$CaCO_3$	Cd(II)	0.9468	122.46	0.032	0.9955	136.52	0.34×10^{-3}
$CaCO_3$	Pb(II)	0.9573	56.67	0.021	0.9973	65.68	0.18×10^{-3}
$CaCO_3$	Cd(II)	0.9431	26.45	0.012	0.9967	30.26	0.12×10^{-3}