Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information

Template-free Synthesis of Hierarchical Porous Calcium Carbonate Microsphere for Efficient Water Treatment

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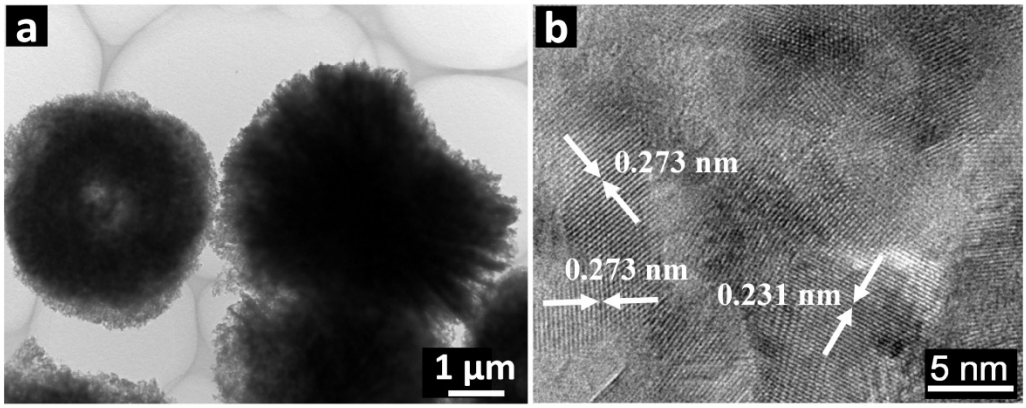

Figure S1. (a) TEM image and (b) HRTEM imag of the hierarchical porous vaterite microspheres, with lattice fringes corresponding to vaterite $CaCO_3$ phase. (d = 0.273 nm, d = 0.231 nm)

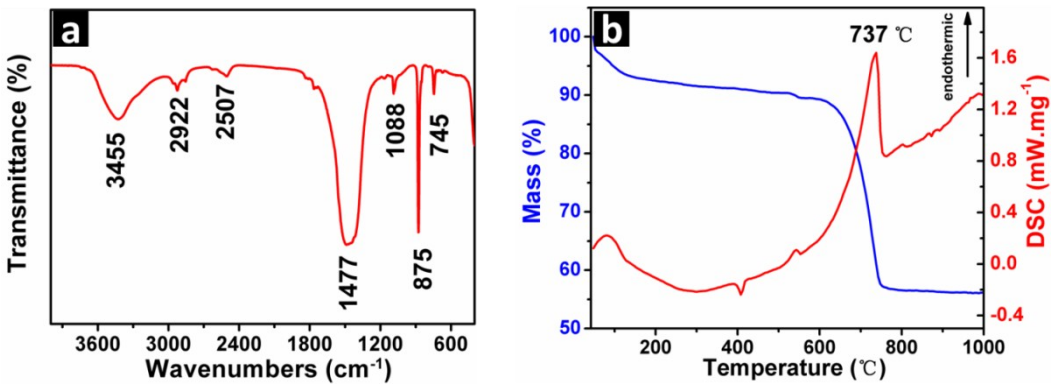

Figure S2. (a) FT-IR spectrum, and (b) TG-DSC curves of the hierarchical porous vaterite microspheres.

The FT-IR spectrum (Figure S1a) confirms the vaterite phase, with absorption bands of 745 cm^{-1}, 875 cm^{-1}, 1088 cm^{-1} and 1477 cm^{-1} for CO_3^{2-} vibration of vaterite. The absorption bands of 2922 cm^{-1} and 2507 cm^{-1} are likely assigned to C-H stretching, and the stretching vibration of N-H in R_2-NH_2^+ or R_3-NH^+, suggesting that there are organic residues in the $CaCO_3$ product. The TG-DSC curves show that water molecules and organic residues exist in the product, with the total weight percentage of around 8.8 %. (calculated by the total weight loss of the product below 560 °C.) The peak at 737 °C corresponds to the decomposition of the sample into CaO and CO_2, which is consistent with previous work.[11]

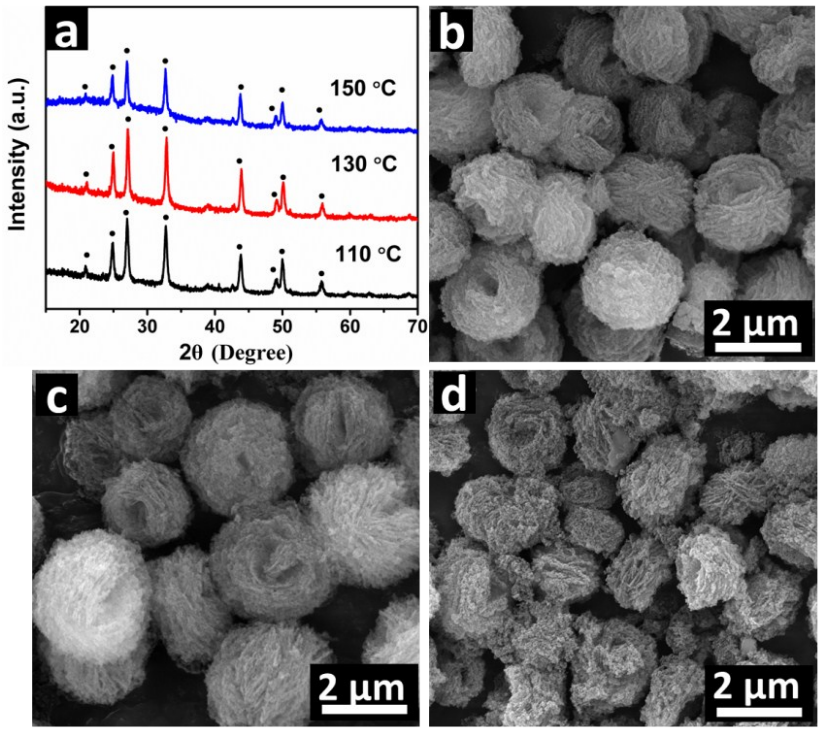

Figure S3. (a) XRD patterns, and (b-d) FESEM image of the hierarchical porous vaterite calcium carbonate microspheres synthesized at (b) 110 °C, (c) 130 °C, and (d) 150 °C for 4h.

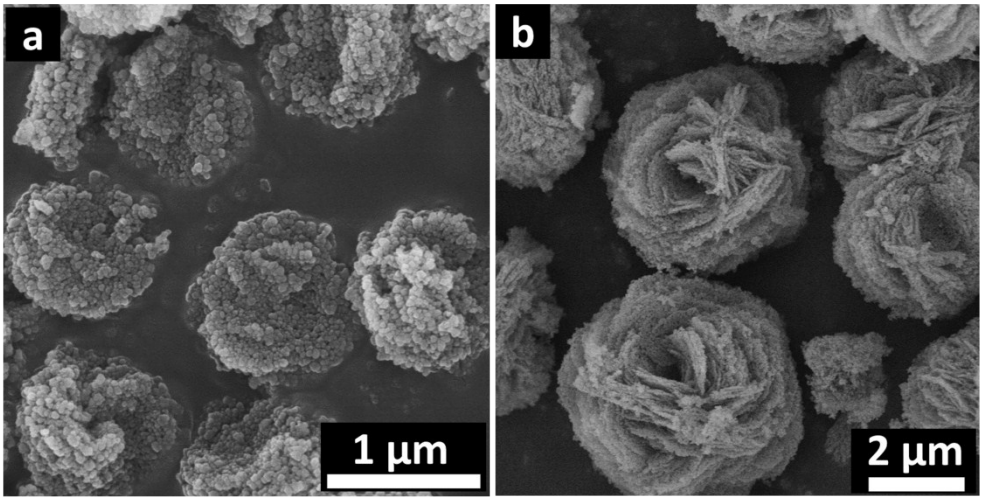

Figure S4. FESEM images of (a) the intermediate particles of the hierarchical porous vaterite $CaCO_3$ microspheres synthesized at 130 °C for 1.75 h, and (b) the matured product after reaction for 4 h.

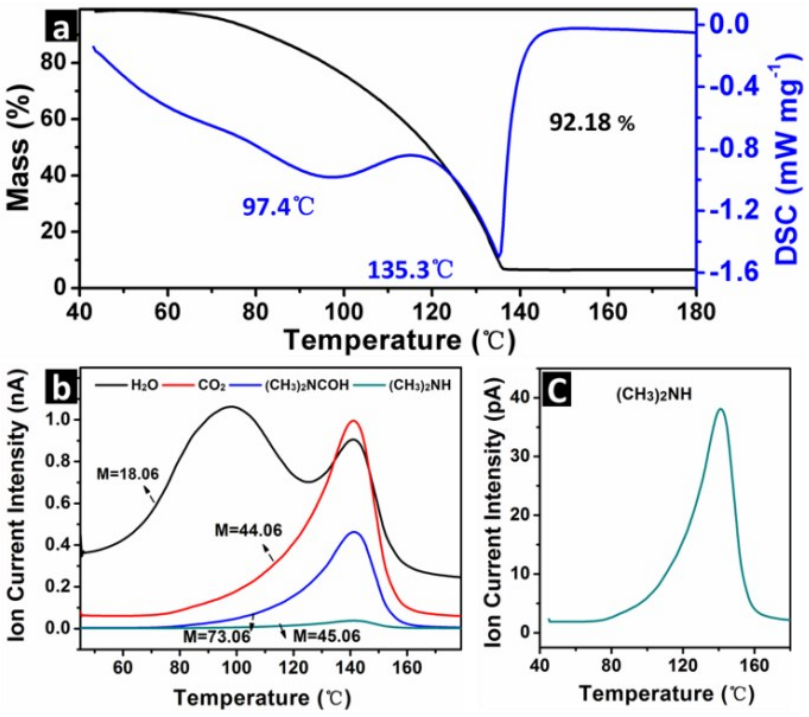

Figure S5. (a) TG-DSC curves, and (b) TG-MS curves of the DMF/H_2O mixed solvents (9:1 v/v) at temperature rising from 40 °C to 180 °C at a heating rate of 5 °C/min. The m/z ion peaks for different curves are 8.15E-10 for H_2O, 9.95E-10 for CO_2, 4.6E-10 for $(CH_3)_2NCOH$, and 3.85E-11 for $(CH_3)_2NH$. (c) the enlarged TG-MS

curve of Figure 3b, which corresponds to the release of the $(CH_3)_2NH$ as temperature increases.

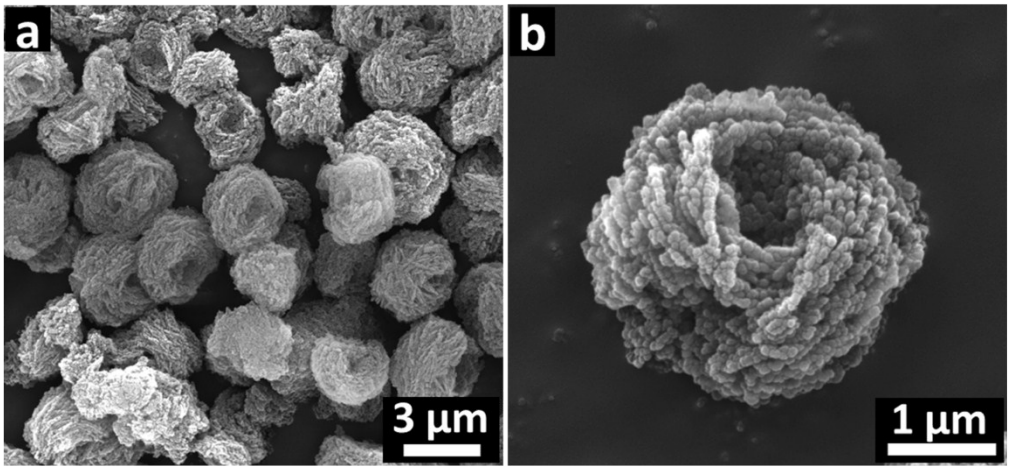

Figure S6. FESM images of the sediments after being treated by the hierarchical porous vaterite microspheres.

Table S1. Adsorption isotherm parameter for the adsorption of Congo red on the hierarchical porous $CaCO_3$ microspheres

Langmuir			Freundlich		
q_m (mg g^{-1})	k_L	R^2	k_f	n	R^2
275.5	0.136	0.994	84.405	4.214	0.833

Table S2. Adsorption kinetic parameter for the adsorption of congo red on the hierarchical porous $CaCO_3$ microspheres

Initial Concentration (mmol L^{-1})	Pseudo-first-order model				Pseudo-second-order model			
	$q_{e,exp}$	$q_{e,cal}$	k_1	R^2	$q_{e,exp}$	$q_{e,cal}$	$k_2(e^{-2})$	R^2

0.1	133.7	132.8	5.421	0.968	133.7	134.2	7.658	>0.99

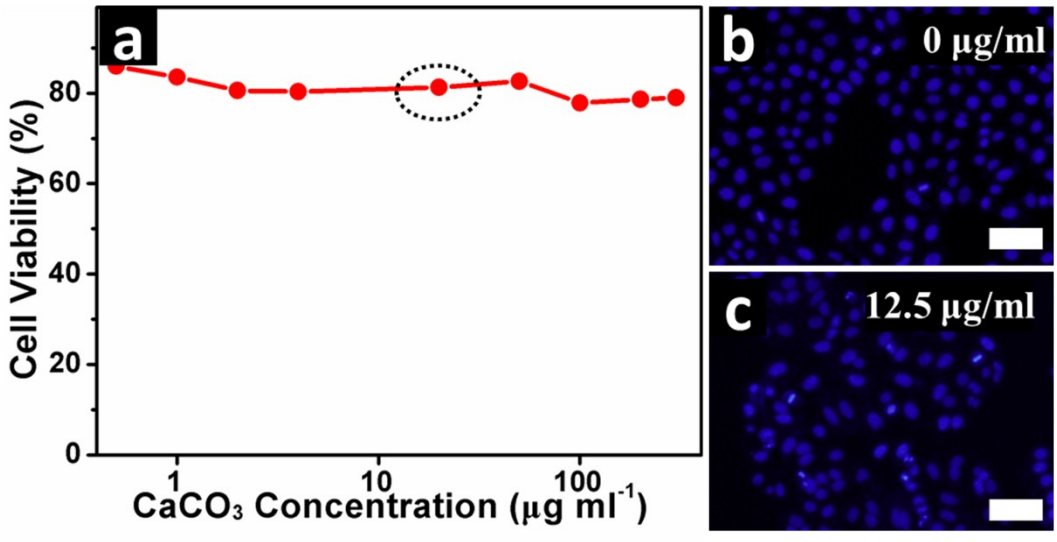

Figure S7. (a) The cytotoxicity towards HepG2 cells after con-incubating with the sample of different concentrations, ranging from 0.15~300 μg ml^{-1}. (b,c) Fluorescence images of HepG2 cells con-incubated with the suspensions of (b) 0 μg ml^{-1} and (c) 12.5 μg ml^{-1} of the sample, corresponding to the star-marked point in Figure 5a. The scale bar inset is 100 μm.

Table S3. Maximum removal capacities of various inorganic adsorbents for Pb^{2+} and Cd^{2+}

Adsorbents	Maximum removal capacity (mg g^{-1})		PH	Reference
	Pb^{2+}	Cd^{2+}		
Hierarchical porous vaterite $CaCO_3$ microsphere	1960	1040	--	Present work
Polyacrylic acid stabilized amorphous calcium carbonate nanoparticles	1028.21	514.62	--	[10]
Polydopamine-functionalized graphene hydrogel	336.32	145.48	6	[30]
Few-layered graphene oxide nanosheets		106.3	6	[33]
Carboxylate-rich carbonaceous materials	351.4	88.8	6	[31]
Nitric acid treated multiwalled carbon nanotubes (CNTs)	97.08	10.86	5	[32]

Table S4. Maximum removal capacities of various inorganic adsorbents for congo red

Adsorbents	Maximum removal capacity (mg g^{-1})	Reference
Hierarchical porous vaterite $CaCO_3$ microsphere	272	Present work
FeOOH hierarchical nanostructures	240	[4]
Urchin-like α-FeOOH hollow spheres	275	[5]
MnO_2 hierarchical hollow nanostructures	80	[34]
Mesoporous Fe_2O_3	53	[35]