Electronic Supplementary Information (ESI)

Magnetic Mesoporous Carbonated Hydroxyapatite Microspheres with Hierarchical Nanostructure for Drug Delivery System

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Preparation of the MHMs

Briefly, Fe_3O_4 nanoparticles (0.2 g) were added into the calcium chloride solution with HCl-soluble nacre materials, followed by ultrasonic treatment for 10 min. Subsequently, the rapid-mixing reaction was performed by pouring the Na_2CO_3 solution into 100 ml of the above mixed solution. The obtained $CaCO_3/Fe_3O_4$ microspheres (0.6 g) were added into a disodium hydrogen phosphate solution. The mixtures were sealed in polytetrafluoroethylene (Teflon)-lined stainless steel autoclaves and hydrothermal transformations took place at 140 1C for 24 h. The obtained products (MHMs) were washed with deionized water, and then dried in a convection oven.

The source and function of HCl-soluble organic materials extracted from the nacre

The nacre of Corbicula fluminea was collected from Zhejiang province in China, composed of 98.1 wt % mineral phases and 1.9 wt % organic components. The chemical elements of nacre mainly include O (48.026 wt.%), Na (0.281 wt.%), Al (0.215 wt.%), Si (0.058 wt.%), S (0.022 wt.%), Ca (40.957 wt.%), Sr (0.083 wt.%), and other elements such as C, H, and N (10.4 wt.%).

The nacre was demineralized with a 1.0 mol/l HCl solution overnight, and diluted with deionized water till the concentration of calcium ions was 0.25 mol/l. After centrifugation and separation from the HCl-insoluble material, the pH-value of the organic calcium chloride ($CaCl_2$) solution was adjusted up to seven by adding a

few drops of 1.0 mol/l NaOH. This yielded a calcium chloride solution, and the organic materials in the solution were termed HCl-soluble organic materials.

In the present work, the HCl-soluble organic materials are used as additive to control the morphology of $CaCO_3/Fe_3O_4$ microspheres. In the absence of the HCl-soluble organic materials, the obtained products are irregular particles. However, the presence of the HCl-soluble organic materials has not obviously effects on the mesoporous structure of the MHMs, as demonstrated by the previous report (Y.P. Guo, et al. Micropor. Mesopor. Mat., 2009, **118**, 480-488;).

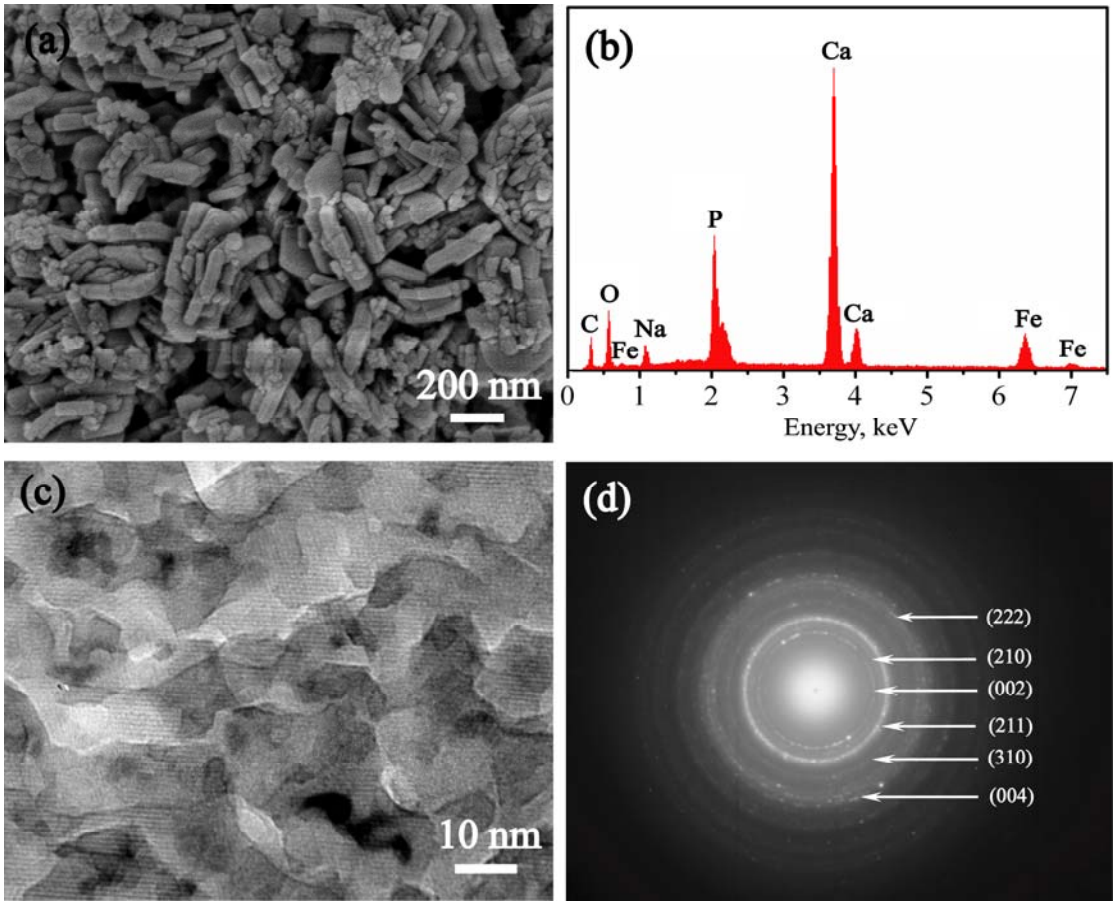

Fig. S1. (a) SEM image with high magnification; (b) EDS spectrum; (c) TEM image; and (d) electron diffraction pattern of MHMs.

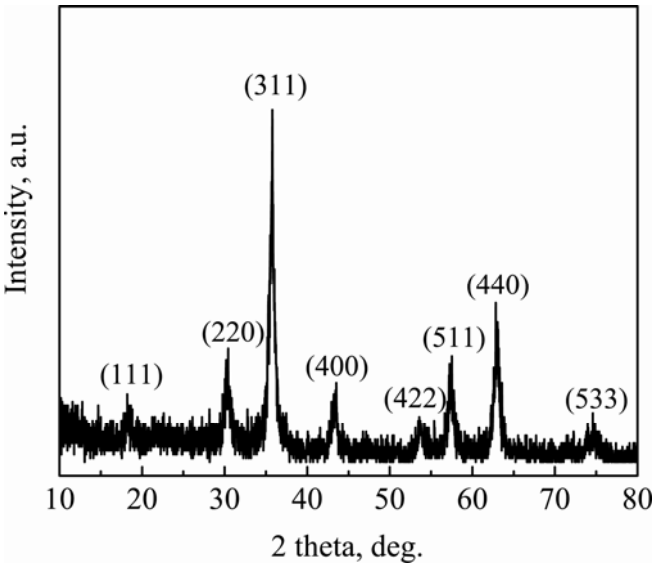

Fig. S2. XRD pattern of Fe_3O_4 nanoparticles.

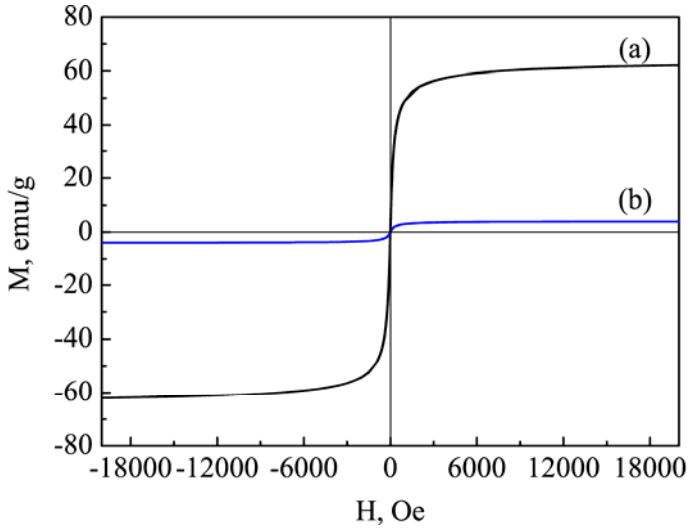

Fig. S3. Magnetization of different samples as a function of the applied field measured at 298 K: (a) Fe_3O_4 and (b) MHMs.

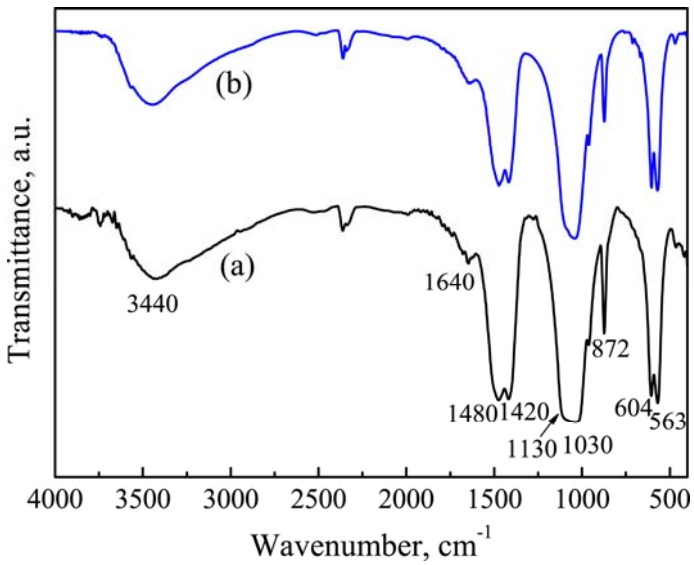

Fig. S4. FTIR spectra of samples: (a) MHMs and (b) HHMs.