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Hierarchically-organized, well-dispersed hydroxyapatite-coated magnetic carbon with combined organics and inorganics removal properties

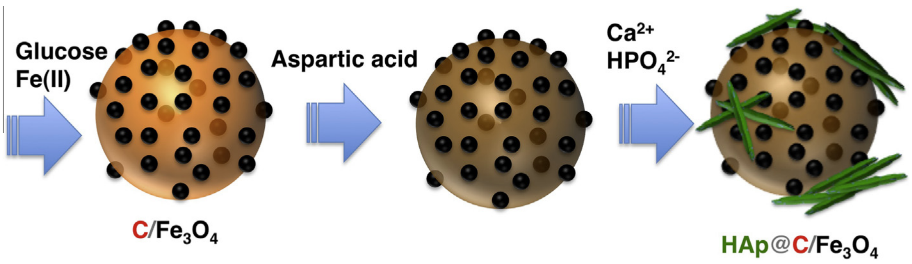
Huihui Yang [a], Qiang Liu [a], Sylvie Masse [b,c], Hao Zhang [a], Laifeng Li [a,*], Thibaud Coradin [b,c,*]

[a] *Key Laboratory of Cryogenics, Technical Institute of Physics and Chemistry, Chinese Academy of Science, Beijing 100190, PR China*
[b] *CNRS, UMR 7574, Chimie de la Matière Condensée de Paris, F-75005 Paris, France*
[c] *Sorbonne Universités, UPMC Univ Paris 06, UMR 7574, Laboratoire de Chimie de la Matière Condensée de Paris, F-75005 Paris, France*

HIGHLIGHTS

- Hierarchically-organized apatite/iron oxide/carbon microspheres were developed.
- The micro/mesoporous powders combine the sorption capacities of carbon and apatite.
- They demonstrate adsorption capacity towards organic and inorganics pollutants.
- These composites can be useful for superconducting separation wastewater treatment.

GRAPHICAL ABSTRACT



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ABSTRACT

Novel hierarchically-organized magnetic microspheres have been successfully developed that consist of an aqueous hollow core, a magnetic porous Fe_3O_4–carbon layer and a well-define hydroxyapatite (HAp) shell. The hollow magnetic carbon microspheres were prepared by ultrasonic spray pyrolysis and coated with HAp using a biomimetic approach. The resulting powders exhibit micro- and meso-porosity. The removal capacity of the composite spheres towards an antibiotic (ampicillin), a rare-earth ion (La^{3+}) and two heavy metals (Hg^{2+} and Pb^{2+}) has been studied and compared with that of the individual components. The dual organic–inorganic affinity of the magnetic HAp/carbon conjugates was demonstrated, with synergetic effects being evidenced for heavy metal removal enlightening their potentialities in wastewater treatment.

1. Introduction

Long-term exposure to polluted waters has significant detrimental effects on human health and, in particular, can cause diseases, such as lungs, bladder, kidneys and skin cancer. The development of low-cost and efficient methods for wastewater treatment is therefore an urgent and highly relevant research area [1–3]. Under normal circumstances, water treatment involves a series of physical, chemical and biological processes [4,5]. A critically time-consuming step is the coagulation/adsorption process where pollutants are precipitated in a particulate form or adsorb on powders as this often requires a subsequent decantation period [6]. Compared to traditional treatment methods, superconducting magnetic separation of sorbents has several advantages, such as the lower investment, smaller area occupied, and shorter period of processing [7,8].

Magnetic materials, named as seeds, play a key dual role in the superconducting magnetic separation technology: they need to

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* Corresponding authors at: Laboratoire de Chimie de la Matière Condensée de Paris, Collège de France, F-75005 Paris, France. Tel.: +86 10 82543698; fax: +86 10 82543700 (L. Li). Tel.: +33 144274018; fax: +33 144271443 (T. Coradin).

E-mail addresses: laifengli@mail.ipc.ac.cn (L. Li), thibaud.coradin@upmc.fr (T. Coradin).

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efficiently immobilize the pollutants and at the same time must be easily separated by application of an external field [9]. Iron and iron oxide nanoparticles are well-suited for this application due to their surface affinity and redox degradation activity towards a wide range of organic and inorganic contaminants [10,11]. To avoid issues related to colloidal stability and handling of nanomaterials, 3D hierarchical nanostructures have been developed [12]. As an alternative, it is possible to design (nano)-composite powders where the magnetic nanoparticles are associated with a sorbent phase [13]. In the field of water remediation, calcium phosphates and carbons represent two important classes of materials with high affinity for inorganic and organic contaminants, respectively [14,15]. HAp and carbon nanoparticles have already been previously individually associated with iron and iron oxide colloids for remediation [16–19]. However, to our knowledge, the corresponding triphasic system organized within a single composite structure has never been described so far.

Looking for a cheap, easily-scalable source of magnetic carbon, we focused our attention on ultrasonic spray pyrolysis (USP) as a continuous, one-step method to obtain porous iron oxide/carbon microspheres [20,21]. The nebulization process is based on the formation of a mist from the aqueous solution under the high-frequency ultrasound radiation. The gas flow carries the droplets into a furnace, where solvent evaporation and precursor decomposition occur, producing the C/Fe_3O_4 composite. In parallel, in order to achieve the controlled integration of the calcium phosphate phase to these microspheres, we applied a biomimetic approach previously developed for the coating of iron oxide particles with HAp [22,23]. This method relies on a pre-coating of a core particle by an acidic aminoacid, followed by addition of calcium and phosphate ions whose precipitation is confined on the particle surface.

Following these approaches, we have prepared here $HAp@C/Fe_3O_4$ core–shell three-phasic composite microspheres. We could evidence that the biomimetic interfacial mineralization allows for confinement of the apatite phase on the microsphere surface. The influence of mineralization on the microsphere porosity and its magnetic properties was studied. The adsorption behavior of bare and coated microspheres towards key pollutants, i.e. the antibiotic ampicillin, La^{3+}, Hg^{2+} and Pb^{2+}, was evaluated and compared. This allows for a discussion of the interplay between the different components within the composite architecture, enlightening their potential applications for water treatment.

2. Material and methods

2.1. Preparation and characterization of $HAp@C/Fe_3O_4$ microspheres

Magnetic carbon microspheres were prepared according to the literature with some modifications [20]. Typically, an aqueous precursor solution was prepared by dissolving glucose (4 g) and ferrous chloride tetrahydrate (3 g) in 100 mL deionized water. The precursor solution was nebulized using a commercially-available household ultrasonic humidifier (1.7 MHz) into a quartz tube placed inside a furnace (700 °C). The flow rate of inert gas (N_2 or Ar) was typically 1 SLPM. The residence time through the furnace was controlled by the gas flow rate and was typically a few seconds. The resulting dark particles were collected into ethanol-filled bubblers and recovered by magnetic separation. These C/Fe_3O_4 products were washed three times with ethanol.

For hydroxyapatite deposition (Fig. 1), 1 g of the C/Fe_3O_4 composite powder was first dispersed into 40 mL of a 1 mol L^{-1} L-aspartic acid solution at 80 °C for 2 h, followed by washing and re-suspension into 40 mL deionized water (sample $C/Fe_3O_4/A$) [23]. In parallel, $Ca(OH)_2$ (0.01 mol, 0.748 g) was dissolved in 100 mL of an ethanol–water mixture (50:50%, v/v) under stirring for 3 h. Then 60 mL of a $NH_4H_2PO_4$ (0.006 mol, 0.67 g) solution was added and the mixture was stirred for 1 h. After this delay, the $C/Fe_3O_4/A$ suspension was quickly transferred into the mixture and the solution was aged for 24 h. The powder was recovered by magnetic separation, thoroughly washed with deionized water and dried at 60 °C under vacuum overnight.

X-ray diffraction (XRD) studies were performed on a Philips PW131 diffractometer, in a 2θ range from 10° to 70°. Transmission Electron Microscopy (TEM) imaging was performed on a JEM-2100, operating at 120 kV. Scanning Electron Microscopy (SEM) imaging was conducted on a Hitachi S-4800, operating at 5 kV. N_2 sorption studies were performed at 77 K using a Quantachrome Quadrasorb SI-MP equipment. Thermogravimetric Analysis (TGA) measurements were performed on a Diamond TG/DTA (Perkin Elmer). Magnetic measurements were performed using a vibrating sample magnetometer (VSM) (Lake Shore 7410) in an applied magnetic field of ±10 kOe at room temperature. X-ray photoelectron spectra (XPS) were recorded on a ESCALAB 250Xi photoelectron spectrometer. The monochromated AlK X-radiation was used as the excitation source.

2.2. Adsorption experiments

Solutions with concentrations ranging from 0 to 5 mmol L^{-1} were prepared from ampicillin (Sigma), $La(NO_3)_3$, $HgCl_2{\cdot}6H_2O$ and $Pb(NO_3)_2{\cdot}6H_2O$ by dissolution in deionized water (pH 6). For kinetics study, 0.2 g of HAp, C/Fe_3O_4 or $HAp@C/Fe_3O_4$ were added to 100 mL of the solutions and stirred with a orbital shaker at 200 rpm at 25 °C. Sorption isotherms were obtained using 0.1 g of the sorbent powders suspended in 50 mL of the contaminated solution and stirred in the same conditions for 24 h at 25 °C. For metal ion solutions, additional experiments were performed at pH = 4 and 8 by addition of HCl and NaOH, respectively. In all

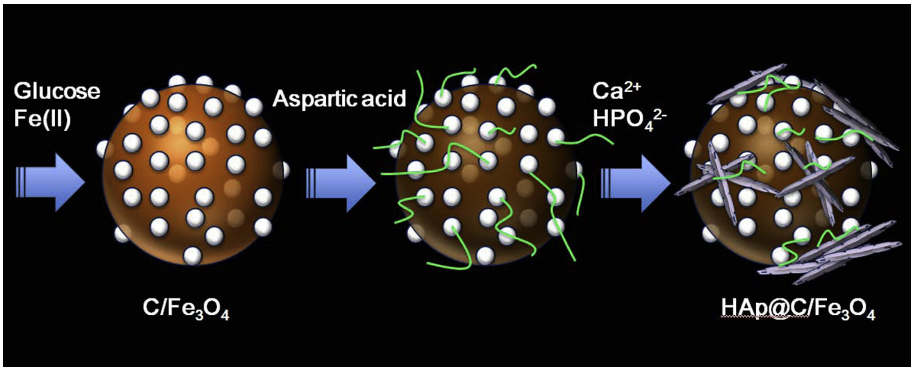

Fig. 1. Overview of the synthetic route to hydroxyapatite-coated magnetic carbon microspheres: carbon microspheres (light brown) decorated with magnetite nanoparticles (white) are first coated with aspartic acid (green), allowing for further deposition of hydroxyapatite nanocrystal (light purple). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)