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2D Magnetic Frames Obtained by the Microwave-Assisted Chemistry Approach

Oana Pascu,^[a] Martí Gich,^[a] Gervasi Herranz,^[a] and Anna Roig*^[a]

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Microwave chemistry is becoming a very attractive synthesis technique in many areas of synthetic chemistry. In particular, the utilization of this method to fabricate nanostructured materials is a fast growing research area with immense potential. Similarly, the use of sacrificial scaffolds has been demonstrated as an effective route to achieve intricate 2D and 3D porous architectures. Here, we present an extremely fast and versatile synthetic approach based on microwave heating to

Introduction

Fabrication of nanostructured materials by using sacrificial scaffolds, against which another material is deposited by mimicking the original template, has been demonstrated as effective and versatile approach towards achieving complex 2D and 3D porous architectures.^[1–2] Among those, 2D or 3D arrays of inorganic hollow spheres can display interesting optical, optoelectronic, magnetic, electric, or catalytic properties.^[3] For such applications, the preservation of the long-range order of the nanostructure is essential. Templating over polymer colloids is a commonly used strategy to achieve long-range order, although it presents the drawback of having to remove the template either by solvent dissolution, etching, or calcination, which in turn could damage the intended hollow structure.

Microwave energy is becoming a very attractive tool in all areas of synthetic chemistry. It has been used not only for organic^[4] and inorganic^[5] nanoparticle synthesis but also for the fabrication of high-quality nanocrystals and large-scale defect-free complex nanostructures with controllable morphologies and surfaces.^[6] Other intricate nanoarchitectures, such as nanoporous materials,^[7] superstructures,^[6] or 3D magneto photonic opals^[8] have also been reported.

In this communication, we describe a facile and fast microwave-assisted sol-gel chemical approach to produce twodimensional hollow magnetic frames using sacrificial templates. The method has allowed us to grow, in just a few minutes, a stoichiometric and homogeneous conformal

 [a] Institut de Ciència de Materials de Barcelona (ICMAB-CSIC) Campus UAB, 08193 Bellaterra, Spain Fax: +34-93-5805729 E-mail: roig@icmab.es fabricate complex macroporous magnetic frames using sacrificial templates. In just a few minutes, a stoichiometric and homogeneous conformal nanometric coating of superparamagnetic nanoparticles was grown onto a 2D monolayer formed by self-assembled polystyrene colloids. No post-treatment was required, the sacrificial polystyrene template was removed simultaneously as the magnetic nanoparticles formed, and large-scale structural order was preserved.

nanometric coating of manganese ferrite on a polystyrene template over an area of half a square centimeter. No post-treatment was required – the sacrificial template is removed simultaneously with the formation of magnetic nanoparticles.

Results and Discussion

The fabrication of complex nanostructures by microwave heating is becoming an area of intense research and great potentiality in synthetic chemistry. In addition to drastically decreasing the time for the synthesis, the technique offers a combination of kinetics and selectivity characteristics that can be used advantageously, such as: (i) the acceleration of the chemical reaction rate, (ii) the heating selectivity - polar substances absorb electromagnetic radiation and are intensively heated while the non-polar ones do not absorb it, and (iii) the high diffusivity of the molecular species in solution facilitates the conformal deposition onto intricate frames. We have recently demonstrated some of those features on the fabrication of three-dimensional magnetic photonic crystals by microwave synthesis, where direct SiO₂ and inverse Al₂O₃ photonic crystals have been uniformly infiltrated with in situ synthesized magnetic oxide nanoparticles.[8]

Here, we describe the conformal coverage with small superparamagnetic $MnFe_2O_4$ nanoparticles of a 2D structure resulting from self-assembled polystyrene (PS) spheres coated with a thin Al_2O_3 layer (10 nm). A schematic representation of the synthesis steps and the resulting magnetic frame is displayed in Scheme 1.

The two-dimensional polystyrene colloidal template, vertically immersed in a solution containing the solvent and the organometallic precursors, was subjected to microwave Date: 05-01-12 14:47:08

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Scheme 1. Schematic representation of the fabrication process.

radiation for a few minutes. The solvent (benzyl alcohol), being a polar substance, absorbs the microwave radiation and increases its temperature, which promotes the decomposition of the organometallic precursor and nanoparticle formation. By coating the PS spheres with a thin layer of an oxide (Al₂O₃ in this case), we gain two additional advantageous effects. Firstly, because PS has a glass transition at about 95-100 °C^[9] and starts melting above this temperature,^[10] the PS template melts during the microwave synthesis at 160 °C and thus the Al₂O₃ frame keeps the mechanical stability of the structure. Secondly, the hydroxy surface terminations of the alumina efficiently absorb the microwave energy, which activates the surface and selectively promotes nucleation and growth of the magnetic nanoparticles on it. Thus, a final 2D hollow structure with a conformal magnetic coating is obtained. When the 2D template is made only of PS spheres, a non polar compound, the coating is not effective, and the template is not mechanically strong during particle deposition.

Prior to the discussion of the characteristics of the magnetic frames, the characterization of the nanoparticles is reported. As explained in the Experimental Section, non-attached MnFe₂O₄ nanoparticles could be separated from the reaction media by adding oleic acid once the reaction had taken place and thus stable colloidal dispersions in hexane were obtained after centrifugation and washing steps.^[11] Transmission electron microscopy (Figure 1a) reveals small nanoparticles with good polydispersity and a rather irregular shape. A size distribution, fitted to a Gaussian function, gives an average size of 4.0 ± 0.8 nm (Figure 1b). The low polydispersity in the distribution of particle sizes is most probably a consequence of the rather uniform formation of nuclei as well as the uniform nanoparticle growth in the microwave reactor. The powder X-ray diffractogram (inset of Figure 1a) and selected area electron diffraction pattern (SADP) (Figure 1c) can be indexed with that of the cubic inverse spinel manganese ferrite phase (ICDD PDF0750035). The magnetic properties of the nanoparticles were evaluated by measuring the magnetization vs. the magnetic field strength at 300 K (Figure 1d) and the zero-field-cooled (ZFC), field-cooled (FC) magnetization curves (Figure 1d inset) vs. temperature. The absence of remnant magnetization at room temperature indicates the superparamagnetic character of the nanoparticles. The low blocking temperature at 26 K corresponds to very small nanoparticles, which is in agreement with the TEM data.



Figure 1. $MnFe_2O_4$ nanoparticles stabilized in organic media. (a) TEM image of monodisperse nanoparticles stabilized with oleic acid; the inset shows the powder X-ray diffratogram of these nanoparicles, (b) size distribution fitted to a Gaussian function, (c) the corresponding electron diffraction pattern, (d) magnetometry data; M(H) at room temperature and ZFC–FC curves at 50 Oe.

With regard to the 2D magnetic frames, the first observation is that the thickness of the coating can be controlled by the duration of the chemical reaction. Scanning electron microscopy (SEM) was used to study the surface of the magnetic frames at different reaction times (Figure 2). The PS template covered by the thin Al_2O_3 shell (about 10 nm) presents a very smooth surface (Figure 2a and inset). The reaction at 160 °C for 2 min results in partial coverage of the template (bright spots on the sphere surface) (Figure 2b and inset). The reaction with the same precursor concentration (0.1 M) at the same temperature (160 °C) but with a 2D Magnetic Frames by the Microwave-Assisted Chemistry Approach



longer reaction time (5 min) produces a complete conformal coating (Figure 2c). Higher magnification (inset of Figure 2c) confirms that the layer is conformal, continuous and consists of small nanoparticles. By increasing the reaction



time to 10 min, the coverage increases to such an extent that the nanostructures are no longer evident and a continuous film is formed instead.

At that point, if the growth continues, every sphere starts pushing against its neighbors, and cracks begin to appear in the nanostructure, as clearly seen in Figure 2d.

The next issue addressed is what happens to the PS template during the chemical reaction that forms the nanoparticles. A close observation of the pristine template reveals that the PS spheres are in contact, and, therefore, the alumina will not be deposited on these contact areas (see Scheme 1 and Figure 2a). Because PS is not very soluble in benzyl alcohol,^[12] we assume that the disappearance of the PS during microwave heating results from a melting process.



Figure 2. The various coverage thicknesses depending on the duration of the chemical reaction are visualized by SEM micrographs. (a) The pristine opal; a higher magnification is included in the inset. (b) Partial magnetic coverage of the opal obtained at 160 °C/2 min; the inset shows one sphere in more detail. (c) Homogeneous magnetic coverage of the 2D template obtained at 160 °C/5 min; the inset shows in better detail the conformal uniform coating as a single sphere. (d) A thick magnetic film is formed at 160 °C/10 min over the 2D template; the inset shows a smaller magnification (scale bar 20 µm) of the film surface.

Figure 3. SEM images of the transversal section across the spheres, which reveals the morphology within the hollow spheres. (a) The material with a bright Al_2O_3 shell (160 °C/2 min); the white spots uniformly distributed on the inner wall are nanoparticles. (b) Spheres with a thicker deposition within the spheres (5 min reaction). The cube inside is made of PS melted and recrystallized during the reaction. (c) After a 10-min chemical reaction under microwaves MW, the PS spheres disappear completely. The white spots inside the spheres are nanoparticle aggregates.

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Since the microwave experiment is a very fast process – the full cycle does not take longer than 15 min - we can also safely assume that the melting of the PS and the nucleation and growth of the nanoparticles occur simultaneously. When the PS melts, the contact areas between two PS spheres become contact windows, which allows the diffusion of the organometallic precursors inside the spheres and consequently the formation of nanoparticles at the inner side of the alumina takes place. This could be verified by the images taken from a transversal section across the templates (Figure 3). In the case of a 2-min reaction, it can be seen that the PS is only partially melted, and a small quantity of nanoparticles uniformly distributed (bright spots) inside the spheres can be observed (Figure 3a). By increasing the reaction time to 5 min, more nanoparticles are deposited on the outer shell and inner shell, a large fraction of the PS is melted, which leaves big voids, and a



Figure 4. EDX spectra for different materials: (a) the template of pristine PS + Al_2O_3 on a glass substrate; (b) magnetic film completely covering the template obtained at 160 °C/10 min; (c-A) spectra corresponding to the template covered by a ferrite layer at 160 °C/5 min. (c-B) spectra for the cube inside the sphere, no Mn and Fe are present.

small fraction of the PS recrystallizes at the center of the spheres in the form of small cubes (Figure 3b).^[13] For a 10min reaction time, the majority of the PS is melted, and large aggregates of nanoparticles accumulate at the center of the sphere (Figure 3c). To certify the coverage of the PS colloidal template with magnetic material, elemental analysis by energy dispersive X-ray spectroscopy (EDX) of the different materials was performed (Figure 4). The spectrum of the pristine template on a glass substrate is displayed in Figure 4a; naturally, iron and manganese peaks are not present. Figure 4b shows the spectrum, obtained at 160 °C over 10 min, of a thick magnetic film that completely covers the template, in which the Fe and Mn peaks are clearly visible. Figure 4c-A corresponds to the spectra (the scanned area represented by the square A of the template covered by a thinner ferrite layer, prepared at 160 °C over 5 min, and the intensity of the Fe and Mn peaks is smaller than in the previous case. Finally, Figure 4c-B corresponds to the spectrum of a cube inside the sphere (marked with a white cross), which reveals that no Mn and Fe is present in this area.

Conclusions

We have reported on a facile, rapid, and inexpensive microwave-assisted approach to fabricate large areas of high– quality, hollow, two-dimensional magnetic frames using sacrificial colloidal templates. We have proved that in addition to short reaction times, the technique offers other characteristics in terms of reaction kinetics, molecular diffusion, and selectivity, which can be used to enhance the potentiality of such a synthetic chemistry approach. The method has allowed the growth, in just a few minutes, of a stoichiometric and homogeneous conformal nanometric manganese ferrite coating of tenths of square millimeters. The coating thickness can be controlled by controlling the time of the reaction. No post-treatment was required – the sacrificial template is removed simultaneously as the magnetic nanoparticle coating is formed.

Experimental Section

Microwave Synthesis: The microwave experiments were carried out by using a CEM Discover reactor (Explorer 12-Hybrid) operating at a frequency of 2.45 GHz and with a power of 200 W. The template, polystyrene beads covered with a thin Al₂O₃ layer grown by atomic layer deposition, self-assembled in one monolayer with an area of 5×5 mm onto a glass slide substrate, were vertically immersed in the reaction solution by using a 10-mL closed pressurized vessel. The reaction media contained the organometallic precursors, iron(III) acetylacetonate [Fe(acaca)₃] and manganese(II) acetate $[Mn(ac)_2]$ (molar ratio of Fe/Mn = 2:1) with a total concentration of 0.1 M in anhydrous benzyl alcohol (1.5 mL). During a typical run, the power was automatically adjusted to heat the sample to 160 °C, and the temperature was kept stable for 2, 5, or 10 min. After the reaction took place, the solution was automatically cooled to 50 °C by compressed nitrogen. The temperature and the pressure were controlled by a volume-independent infrared sensor.

2D Magnetic Frames by the Microwave-Assisted Chemistry Approach

The Al₂O₃ layer was deposited by ALD (Savanah 100 system by Cambridge Nanotech). Reactants for alumina growth, i.e. trimethylaluminum (TMA) and water were kept at room temperature. The PS monolayer was placed in the ALD chamber at 100 °C, under a N2 flow of 20 sccm and exposed to continuous TMA and water pulses (0.15 s each). Every TMA/water cycle was followed by a waiting time of 8 s, to ensure the complete reaction of the species on the exposed surface of the sample. Hundred cycles were performed as the rate of alumina growth is about 0.1 nm per cycle, which yields an alumina layer of 10 nm. Non-attached nanoparticles were also separated from the reaction media. Briefly, the reaction solution was mixed with excess EtOH (in a volume ratio of 1:3) and surfactant (20 µL, oleic acid for organic dispersion) followed by centrifugation at 6000 rpm for 30 min. The supernatant was discharged, and the precipitate redispersed in hexane (2 mL) containing oleic acid (10 µL) followed by centrifugation at 6000 rpm for 15 min. No precipitate was separated, and the stable dark brown solution was used for further analysis.

Material Characterization: TEM micrographs were obtained with a JEOL JEM-1210 electron microscope, operating at 120 kV. The selected area diffraction patterns were captured by using a JEOL JEM-2011, operating at 200 kV. The samples were prepared by depositing a drop of diluted nanoparticle dispersion in hexane onto a TEM grid and by letting the solvent evaporate. The mean diameter and polydispersity of each system were determined by fitting a particle size histogram of over 200 counts measured from TEM images to a Gaussian distribution by using the imageJ software. Template SEM images were acquired by using a Quanta FEI 200F microscope in low vacuum mode with a cone LOW kV P.L.A. with a 500-µm aperture. The working conditions were: acceleration voltage 5 kV, electron beam spot 2, pressure 40 Pa, and distance 5-6 mm. For the EDX analysis, 10-15 kV, a spot of 2.5-3, and a distance of 10 mm were used. Magnetic characterization was performed with a quantum interference device (SQUID) magnetometer (Quantum Design MPMS5XL). The sample was prepared by using a gelatin capsule filled with compacted cotton impregnated with 150 μ L of a hexane dispersion of nanoparticles, which gave a mass of 1.2 mg (magnetic material without surfactant).

Acknowledgments

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The fabrication of porous magnetic nanoarchitectures by microwave heating is reported. In addition to drastically decreasing the time for the synthesis, other characteristics of the technique, i.e. reaction kinetics, diffusivity and selectivity, have been exploited.

Porous Magnetic Nanoparticles

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A.	Roig*		••••••		•••••	1–7

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