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Colloidal photonic crystals obtained by the Langmuir–Blodgett technique

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Abstract

Monodispersed silica spheres with diameters of 220–1100 nm were prepared by hydrolysis of tetraethyl orthosilicate (TEOS) in an alcoholic medium in the presence of water and ammonia. By grafting vinyl or amine groups on silica surfaces using the coupling agents allyltrimethoxysilane and aminopropyltriethoxysilane, respectively, amphiphilic silica spheres were obtained and could be organized to form a stable Langmuir film at the air–water interface. The control led transfer of this monolayer of particles onto a solid substrate gave us the ability to build three-dimensional regular crystals with well-defined thickness and organization. These colloidal crystals diffract light in the UV, visible and the near-infrared (NIR) spectral regions, depending on the size of the silica spheres and according to the Bragg's law.

Keywords: Colloidal crystals; Silica; Langmuir–Blodgett technique; Controlled architecture

1. Introduction

For many years, colloidal crystals have drawn a considerable interest in the field of materials chemistry, both for theoretical and experimental considerations. Such nanostructured materials, consisted of a controlled assembly of monodisperse colloids in a highly regular structure (typically a face-centered cubic system), are indeed particularly interesting and perfectly adequate for the field of photonic crystals, i.e. dielectric materials with a one-, two- or three-dimensional periodicity exhibiting peculiar interactions with light [1–4]. Several techniques have been developed for the creation of such materials, including colloidal self-assembly [5–10], 3D holography using multiple laser beams [11,12] and photolithography [13]. We have previously reported that colloidal crystals with a thickness controlled at the layer level can be synthesized by using the well-known Langmuir–Blodgett technique [14]. Here we report the elaboration of crystals with a perfectly controlled thickness starting with silica spheres with diameters ranging from 220 to 1100 nm, in order to elaborate SiO_2 photonic crystals with diffraction wavelengths going from 500 to 2300 nm. In fact, it is the first report of the synthesis of high optical quality crystalline

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spheres arrays with a well-defined thickness which operate in the near-infrared region, that is a challenge to fabricate practical optical devices for telecommunications. Reese and Asher [15] and Hamilton coworkers [16] have previously reported the elaboration of such materials but without the control of their thickness at the layer level.

2. Experimental

2.1. Materials

Tetraethoxysilane (TEOS, Fluka), ammonia (29% in water, J.T. Baker), allyltrimethoxysilane (Gelest-ABCR), aminopropyltriethoxysilane (Aldrich) were purchased in their reagent grade and used without further purification. Deionized water was obtained with a MilliQ system (Millipore) whereas ethanol (EtOH), methanol (MeOH) and chloroform ($CHCl_3$) were purchased from Prolabo.

2.2. Methods

2.2.1. Synthesis of silica particles

The methods employed for the synthesis and the functionalization of silica particles were similar to those described in a previous work where the syntheses of particles with diameters of 460 and 680 nm were detailed [14]. The amounts of reagents solutions employed for the synthesis of spheres of other diameters in the micron size range are given in Table 1. In some experiments, an alcoholic solution of TEOS was prepared separately and introduced continuously in the medium at a precise rate thanks to a single-syringe pump (see below).

2.2.2. Functionalization of silica particles

Allyltrimethoxysilane or aminopropyltriethoxysilane was directly added into the nanoparticles dispersion. The amount of coupling agent was around ten times higher than the amount necessary to cover the inorganic surface with a monolayer (the theoretical amount for such a coverage being nominally 2 molecules nm^{-2}). After it was left to react overnight, the mixture was held at 80 °C for 1 h to promote covalent bonding of the organosilane to the surface of the silica nanoparticles. The choice of allyltrimethoxysilane and aminopropyltriethoxysilane was driven by the necessity to avoid the aggregation of the silica particles either in solution before their spreading at the air–water interface or just after this step.

2.2.3. Silica suspensions treatment

In order to eliminate the remaining reagents, all the suspensions were dialyzed against water several times (for a small particle size) or submitted to several cycles of washing and centrifugation. The final concentration of the suspension was determined by measuring the mass of a dried extract and the measured value was always in agreement with the theoretical one (calculated assuming a complete conversion of TEOS into silica).

2.2.4. Silica particles size measurements

Granulometry experiments were performed on a Malvern Mastersizer apparatus.

2.2.5. Formation of a 2D-array of particles

A diluted suspension of functionalized silica particles in a 80%/20% (v/v) mixture of chloroform and ethanol was prepared according to a previously reported procedure [14]. After spreading on a pure water subphase (pH = 5.5), a stepwise compression of the 2D

Table 1
Experimental conditions corresponding to the synthesis of silica spheres with various diameters

Reaction medium		Solution of TEOS		Rate of addition ($mL\ h^{-1}$)	Final particle size (nm)
Volume of alcohol (mL)	Volume of ammonia (mL)	Volume of alcohol (mL)	Volume of TEOS (mL)		
200 (EtOH)	15	0	5	[a]	220
100 (MeOH)	20	20 (MeOH)	20	20	360
200 (EtOH)	20	25 (EtOH)	25	8	1100

[a] TEOS was added at once.