Mesoporous films are a fine example of a self-assembled nanosystem, containing ordered porosity in the 2–50 nm range. A great number of characteristics, including framework nature (composition, crystallinity), high surface area, pore dimension, shape, surface, accessibility and pore array symmetry and interconnection can be tuned using green chemistry synthetic techniques. These materials present potentials in several fields where a large functional interfacial area contained in a robust framework is required. The capability of changing in a separate way the characteristics of the inorganic framework and the pore surface leads to an amazing potential in tuning functional properties, due to the combined properties of a thoroughly tailored pore system and the inherent features of thin films. These properties can be tailored to respond to changes in the environment, such as relative humidity, making mesoporous hybrid thin films an exciting prospect for several nanotechnology applications (e.g. sensors, actuators, separation devices). Here we present some basic concepts revolving around mesoporous films. We will first comment on the synthetic approach in the fabrication of these materials. Second, we will discuss the aspects regarding template organization and surface functionalization. Third, we will review some applications illustrating the potentialities of these self-assembled nanomaterials.
Keywords: Mesoporous, thin-films, self-assembly, sol-gel.

1. Sol-Gel Chemistry, Self-Assembly and Mesoporous Thin Films

1.1. INTRODUCTION

Sol-gel processing is a low temperature synthesis route that is particularly suitable for the deposition of thin films from a liquid phase. The high versatility of the technique has allowed a wide diffusion in different fields of applications and several products are now on the market. The soft chemistry approach of sol-gel has known a renewed interest because of the recent boom of nano-science; sol-gel processing has emerged as one of the most interesting routes to bottom-up preparation of nanomaterials, nanoparticles and surface functionalization of nanostructures.

Two main different approaches to sol-gel nanochemistry can be envisaged. In the first one sol-gel reactions are used to obtain interconnected structures through polycondensation of the precursors, which is the typical bottom-up route for thin and ultra-thin film preparation. In the second one the final material is obtained through an intermediate step by using sol-gel chemistry for the synthesis of nano-objects, such as nanoparticles or nano-building blocks (NBBs). Sol-gel chemistry can be, however, also combined with more sophisticated nano-synthesis techniques to get ordered and hierarchical structures. Controlled porosity in a material can be achieved, for instance, by templates that are removed after the preparation; templates of different dimensions can give hierarchical porous materials. Porosity in the nano-scale is an important property of a material that should find its field of applications in nanotechnologies.

Micro- (<2 nm), meso- (2–50 nm) and macro-porosity (>50 nm) can be used to entrap organic functional molecules, to create nanoreactors or as host for nanoparticles. The properties of porous materials can be greatly enhanced if an organized and interconnected porous “structure” is obtained, in this case diffusion, adsorption and entrapping of functional molecules are favored and the material can reach a high level of sophistication. Mesoporous ordered materials are an important example of this type of nano-engineered materials whose synthesis is achieved through a combination of sol-gel and supramolecular chemistry. The formation of an organized array of pores, whose topology, size and distribution is controlled by the processing parameters, is obtained through a self-assembly process. Amphiphilic molecules, such as ionic surfactants and block copolymers, are used to generate organic micelles that serve as the templates; removal of the micelles leaves ordered pores (Figure 1).