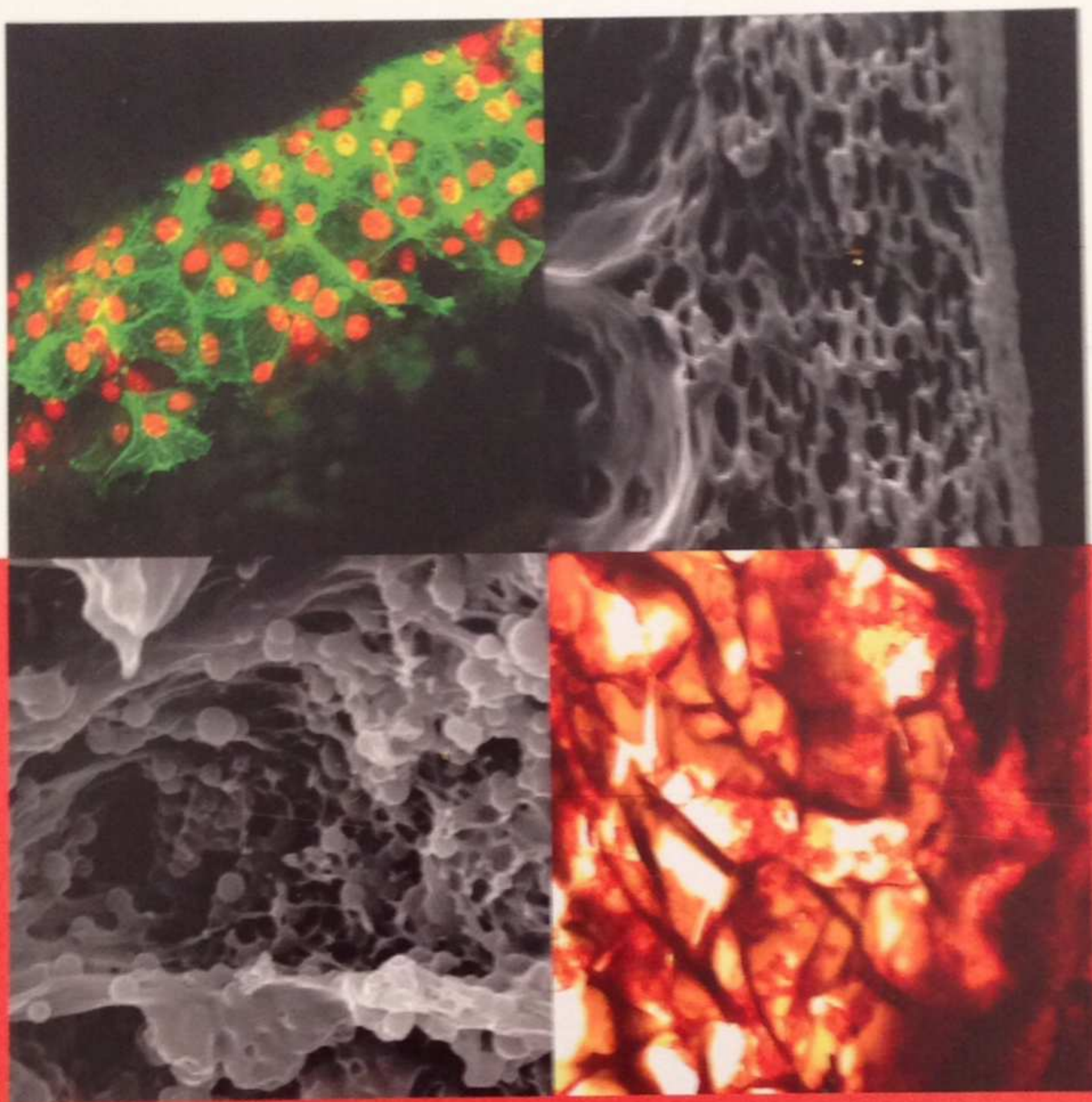


# I MATERIALI BIOCOMPATIBILI PER LA MEDICINA

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Convegno Nazionale della Società Italiana Biomateriali  
Palermo, 2-4 luglio 2014



*a cura di*

Riccardo Alessandro  
Valerio Brucato  
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Giuseppe Spadaro



UNIVERSITÀ  
DEGLI STUDI  
DI PALERMO







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### Introduction

Chemical sensing using optical devices has been the subject of extensive research during last decades and optical chemical sensors are finding increasing applications in industry, environmental monitoring, medicine, biomedicine and chemical analysis.

Optical chemical sensors have several advantages over conventional electricity-based sensors, in terms of selectivity, immunity to electromagnetic interference, higher sensitivity, and they are also relatively inexpensive and minimally invasive. An emerging class of optical chemical sensors is based on Inverse Photonic Crystals (IPCs) based on responsive-hydrogels<sup>1-3</sup>. In these systems, the structural color due to coherent light scattering from wavelength-scale ordered porosity in the hydrogel confers a broad capacity for color tuning in response to an external stimulus. Hydrogels have been engineered to change their shape, volume or density as a response to changes in temperature, applied magnetic fields, UV light, applied mechanical strains, interaction with specific molecules and biomolecules<sup>4-8</sup>, etc. Structural color in hydrogel-based IPCs is tied to the changes in the physical properties of the hydrogel forming the structure, that affects, in turn, the refractive index mismatch between material and air, and/or the characteristic pore size or pitch of the photonic structure<sup>1-3</sup>.

In this work, we report on the synthesis and optical characterization of a polystyrene (PS) opal, infiltrated with a stimuli responsive hydrogel formulated to be sensitive to ethanol in mixture with water, both in the liquid and in the vapor phase. The PS opal structure used a template was generated through the self-assembly of PS nanoparticles onto glass slides immersed into a PS nanoparticles aqueous dispersion, upon solvent evaporation. The template was infiltrated with the monomers and cross-linker selected to generate *in-situ* the ethanol-responsive hydrogel through UV-photo-crosslinking, followed by a thermal post-cure. The optical properties of the responsive Infiltrated Photonic Crystals as function of ethanol concentration were investigated. Significant shifts of the photonic band gap were observed at the variance of ethanol concentration.

### Materials and Methods

Self-assembly of nanoparticles was carried out using a commercial dispersion of monodisperse polystyrene nanoparticles (Polysciences, 0.3 wt% solid content) with an average diameter of 220 nm ( $\pm 5\%$ ). The 3D close-packed array of polymer nanoparticles was grown onto glass slides through a solvent evaporation induced vertical deposition method<sup>10,11</sup>.

Periodic arrangement of the Photonic Crystals and Inverse Photonic Crystals (IPCs) (Figure 1 a-b) was observed by scanning electron microscopy analysis carried out by a Philips 505 Quanta 200 ESEM FEG.

Hydrogels are composed by 2-hydroxyethyl methacrylate (HEMA), acrylic acid (AA) and poly(ethylene glycol)200 dimethacrylate (PEG200DMA), all from Sigma Aldrich. Azobis-isobutyronitrile (AIBN) was used as initiator at 0.15% wt/vol. Small droplets of monomers aqueous solution were dropped on the top-edge of the direct photonic crystal deposit. The mixture was cured with a UV irradiator from Helios Italquarz "Polymer 125 UV", equipped with a high-pressure Hg lamp "Zp-type" (2 mW/cm<sup>2</sup>). After photo-curing, a thermal post-curing treatment in an oven at 70 °C for further 2 h was carried out. In order to perform the optical characterization of the samples, we used the set-up described in detail elsewhere<sup>11</sup>. Transmission measurements were performed in the 400–700 nm range with a wavelength step of 0.5 nm, dividing the transmitted power by the incident one.



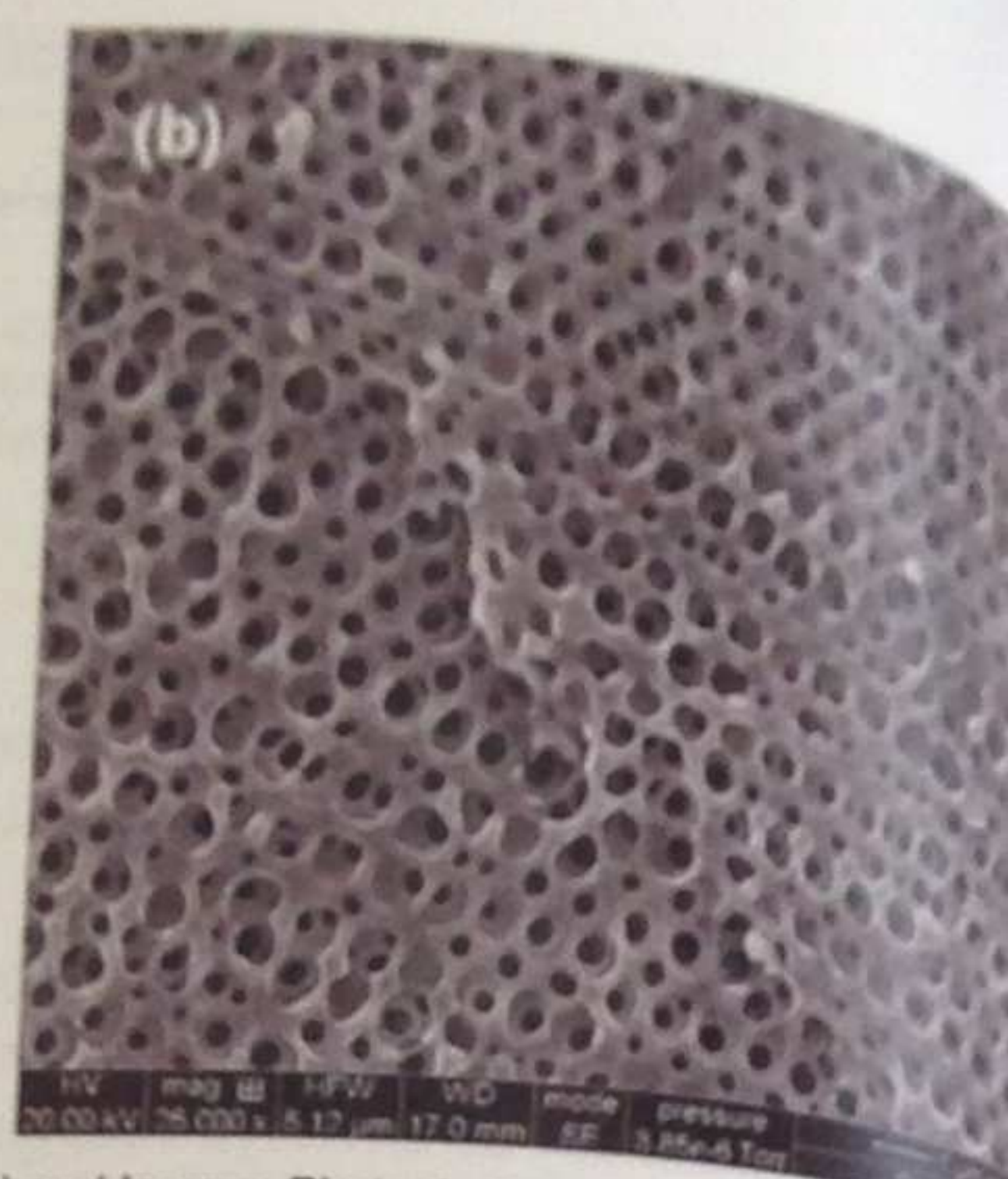
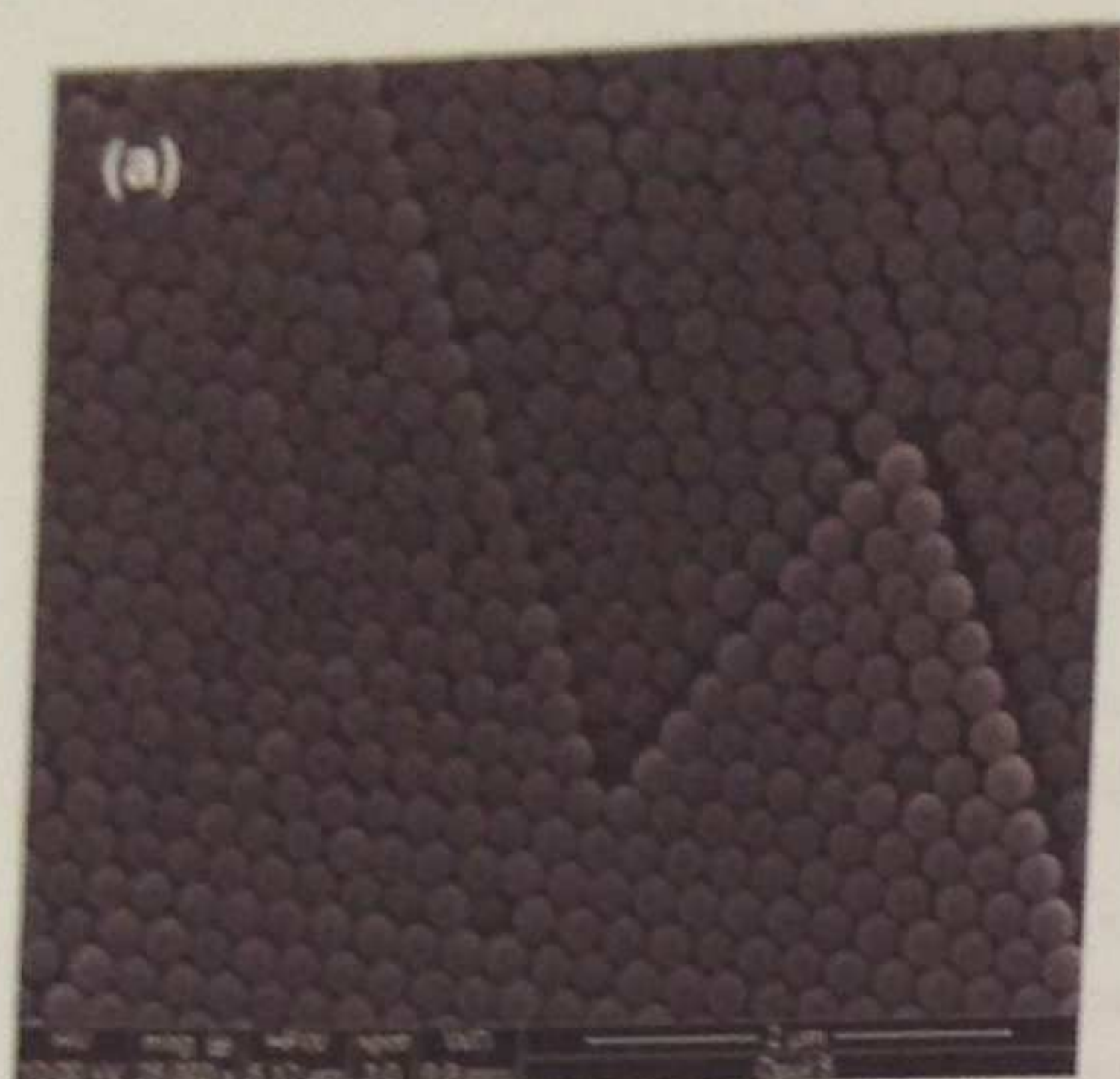


Fig. 1. SEM micrograph of the Photonic Crystals (a) and Inverse Photonic Crystals (IPCs) (b).

### Results and Discussion

Networks of 2-hydroxyethyl methacrylate-co-acrylic acid (HEMA-co-AA) were synthesized to create hydrogels that are able to uptake water and also show significant incremental swelling when exposed to ethanol, after being equilibrated with water. The swelling behavior in the presence of other organic solvents, such as methanol or acetone, was significantly different<sup>12</sup>.

When HEMA-co-AA hydrogels were polymerized within the interstitial spaces of a polystyrene colloidal crystal, mesoscopically structured, periodic films were obtained, which Bragg diffracted light in the visible portion of the spectrum.

It was observed that the infiltration process of the hydrogel in the interstitial spaces of the PS colloidal crystal did not alter its periodic structure and the Bragg resonance peak at normal incidence was shifted from 505 nm, for the Photonic Crystals, to 540 nm, as a result of the increase in spacing after hydrogel infiltration<sup>11</sup>.

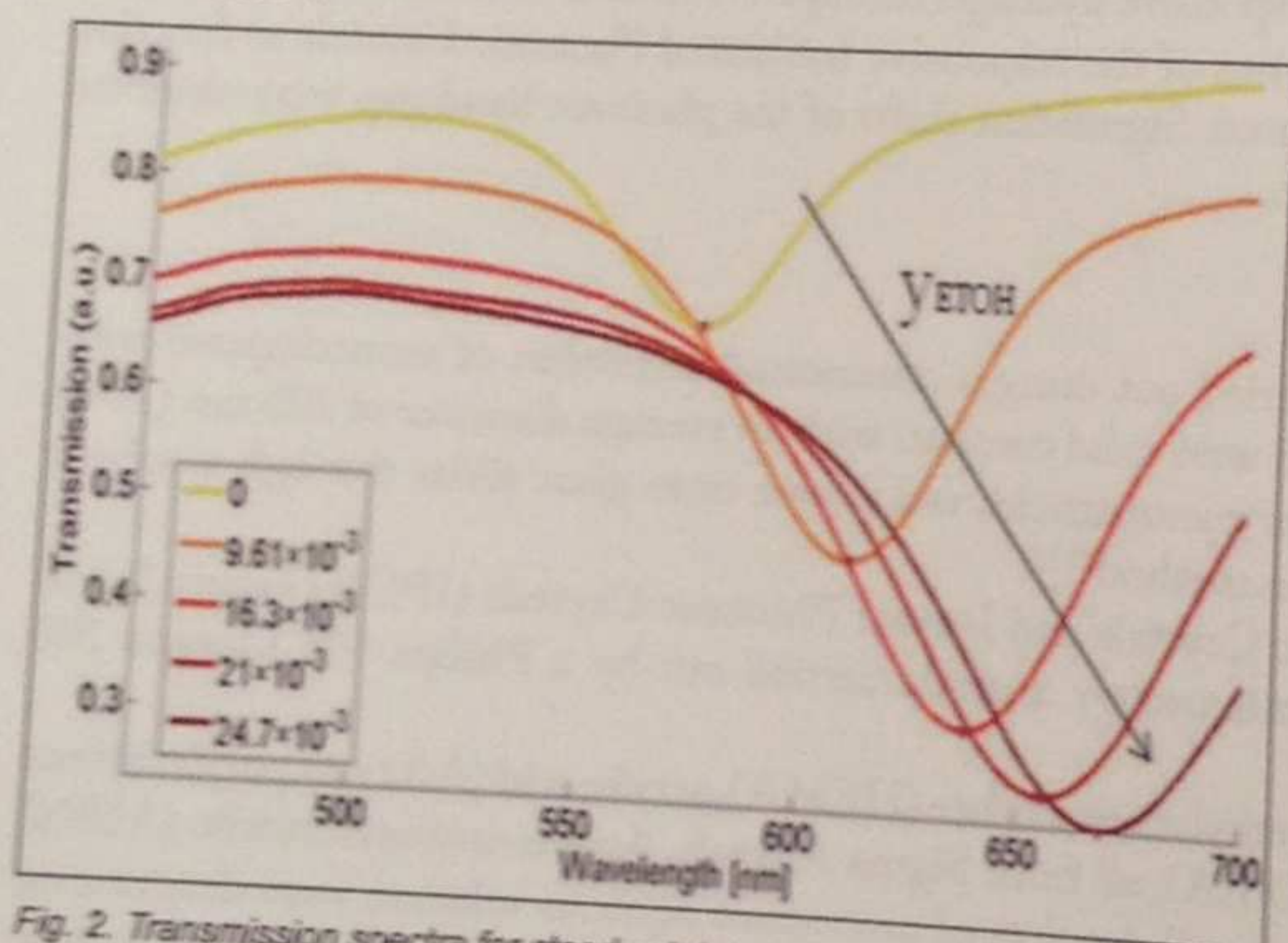


Fig. 2. Transmission spectra for steady-state conditions at the increase of concentrations of ethanol vapor in the atmosphere.

The optical characterization of the hydrogel infiltrated photonic crystals, when exposed to water and ethanol phases and at different water/ethanol concentrations, showed significant Bragg diffraction peak shifts. The film exposed to ethanol changed color from iridescent green to red and reversed to green when no longer exposed to ethanol. The increase of Bragg diffraction peak corresponded to the increase of crystal lattice distance of polystyrene nanoparticles as a result of hydrogel swelling.

In Figure 2 the optical transmission spectra at the different ethanol mole fractions in vapor phase in the steady-state conditions is shown. A linear response both in the Bragg peak wavelength and in the swelling ratio, as a function of the mole fraction of ethanol present in the atmosphere, is observed<sup>11,12</sup>. The linearity of the shift of Bragg peak wavelength of the diffracted light is directly related to the linearity of



swelling degree modification in this concentration range, since the swelling process changes the mean separation between the colloidal particles in the infiltrated opal and, thus, the Bragg diffraction peak position. Response time is fairly long and of the order of few minutes. The Bragg shifts associated to the hydrogel swelling are reversible<sup>11,12</sup>.

Current development of this research is devoted to explore the lower concentration range of ethanol and increase the response time by removing the polystyrene template.

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