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Colloidal crystals: A suitable tool for the development of nanoscale responsive structures

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Summary. — In this work, we report on a colloidal composite system based on polystyrene nanoparticles embedded in an elastomeric matrix able to change its color in presence of different solvents and their mixtures. The structure presents an iridescent green color that can be attributed to the ordered assembly of the constituting nanoparticles causing the formation of a pseudo band gap. The composites realized present a colorimetric variation in their response, since a remarkable blue-shift of the diffraction peak is observed. The selectivity and sensitivity of the responsive system have been investigated by monitoring the static and dynamic reflectance spectra considering different solvents and a mixture of tert-butyl alcohol and water. An analytical model has been proposed and validated in order to assess the optical chromatic response, investigating the variation in frequency of the diffraction peak as well as the filling factor. The prepared structure and the interrogation approach can be seen as a suitable tool for the development of low cost portable and visual sensors for homologues and mixtures.

1. – Introduction

Since photonic crystals (PCs) were introduced by Yablonovich [1] and John [2] in 1987, researchers have attempted to fabricate PC materials with photonic band gaps (PBGs) [3,4]. In fact PCs are structures having spatial architectures (1D, 2D and/or 3D) with a periodically changing complex dielectric function at scales comparable to wavelengths of light in demanded frequency range. Consequently, the periodical distribution of complex dielectric function leads to appearance of distinct regions in the dispersion spectrum, where photons are either allowed or forbidden to propagate, *i.e.*, formation of photonic bandgap. The PBG structures show some intriguing optical phenomena such as strong localization of photons, theoretically lossless sharp bending of light direction, suppression or enhancement of light emission [1]. So far, there have been reports on a large variety of preparation techniques for 3D PC structures, either the top-down methods such as lithography and selective etching [5,6], multi-photon polymerization [7], and holography [8] or the bottom-up methods such as colloidal growth [9-11]. Recently, highly ordered colloidal crystal (CC) photonic films of silica or polymers have been of

growing interest because of their applicable optical properties and low-cost fabrication possibilities by spontaneous self-assembly from suspension media. The self assembly of microparticles into the face-centered cubic (fcc) lattice enables fabrication of large area 3D opal structures. The PBG of uniform colloidal crystal behaves optically as the Bragg reflector in visible or near IR spectral regions, if the particles diameter ranges within few hundreds of nanometers. A variety of methods, such as gravity sedimentation [12], electrostatic repulsion [13], capillary forces induced convective self assembly (Vertical deposition (VD)) [14], and electric field induced assembly [15], have been developed to create colloidal crystals in a time period from days to weeks. Among the above techniques VD is nowadays the most widely used, it is based on the evaporation of the liquid forcing the spheres to arrange in the meniscus formed between a vertical substrate, the suspension and air. This method provides precise control over the thickness with superior crystalline quality of the structures even for diameters larger than $1\,\mu$m [16]. PCs, inspired by photonic materials with vivid structural colors common in Nature and found in species of birds, butterflies, insects, marine life, and even flora, have been developed as chromatic structures for colorimetric sensors. These systems are created by combining the features of colloidal crystals with suitable materials that are responsive to external stimuli [17] such as solvents [18, 19], temperature [20, 21], pH [22], humidity [23], and mechanical force [24]. Generally, PC sensors are constructed using responsive photonic crystals (RPCs) that change their photonic structures and reflection signals under external stimuli. Because of the tunable crystal structure and optical signal under external stimuli or in different environment, the RPCs are intrinsically suitable for portable and visually detectable sensors. From an application point of view colloidal crystals have been extensively explored due to their important applications such as photonic paper [25], anticounterfeiting [26], displays [27], and chemical and biological sensors [28-30]. Among these applications, PC sensors have been used to detect different analytes such as organic solvents [31-33] or gases and volatile organic compounds [34]. The determination of water in organic solvents is of the highest significance in industry, for example the pharmaceutical and chemical ones, as the presence of water not only disfavours the production of chemical and drugs, but also reduces the efficiency of drugs and the usefulness of chemical products. In fact, the employment of alcohols and alcohol/water mixtures in the field of pharmaceutical processes represents a solution in case of hydrophobic and insoluble active principle ingredients that cannot be freeze dried adequately with water-based formulations [35]. Tert-butyl alcohol and its water mixtures have been used in many pharmaceutical processes, the control of the composition of the mixture is one of the main freezing parameters that heavily affects the final results in terms of solubility, sublimation rates and times, costs and product stability [36]. In this contest the development of inexpensive, rapid and portable methods to distinguish between different solvents and to determine water in alcohols is greatly needed. In this paper we report an easy and practical method for the fabrication of composite colloidal crystals based on PS nanoparticles embedded in an elastomeric matrix such as polydimethylsiloxane (PDMS) which is optically responsive to solvents and alcohol/water mixtures. Starting from the experimental data, an analytical model has been proposed and validated in order to assess the chromatic response of the colloidal crystal, making the assumption of an isotropic displacement of the spheres assembled in the periodic lattice fcc of the colloidal crystals.
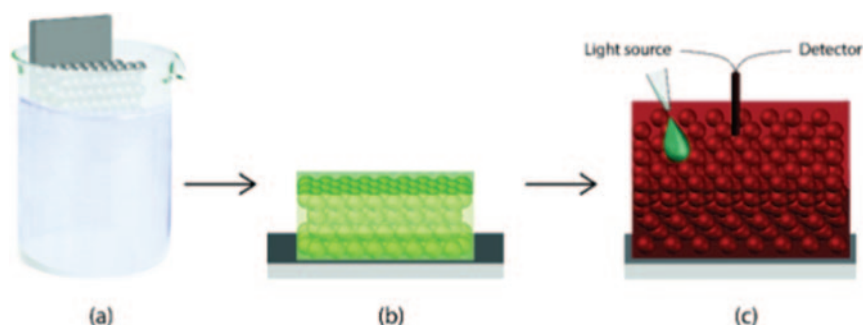
Fig. 1. – (a) assembly of the colloidal structure by VD technique (b) infiltration with responsive material (PDMS) (c) detection of the analytes by composite structure.

2. – Experimental

2˙1. *Chemicals*. – Styrene monomer (SM), sodium dodecyl sulfate (SDS), potassium persulfate (KPS), sodium hydroxide (NaOH), ethylene glycol (EG), tert-butyl alcohol (tert-BuOH), ethanol (EtOH), methanol (MeOH) were purchased from Aldrich. Sylgard 184 (PDMS) and silicon fluids 1cSt and 10cSt were purchased from Dow Corning. Polyethylene terephthalate (PET) sheet was purchased from Polymer House and used as polymeric substrate.

2˙2. *Synthesis of monodisperse latex particles*. – Latex spheres (PS NPs) have been synthesized according to a single-stage polymerization process [37]. All chemicals were used as received, except SM that was washed three times with an equal volume of 1M NaOH and then with water to remove the polymerization inhibitor. The polymerization process was conducted in a 500 ml glass reactor equipped with a stirrer, a reflux condenser and a heating jacket. Briefly, 245ml of distilled water, 0.081 g of SDS dissolved in 13.6 ml of water and 27.2 ml of purified SM, were premixed in the reactor at the temperature of 80 °C for 2 min. and at a stirrer speed of 300 rpm. To start the polymerization an amount of 0.952 g of KPS dissolved in 13.6 ml of water was injected. The reaction was stopped after 4 h and after cooling down the colloidal solution was purified by repeated washing with water and centrifugation/redispersion cycles.

2˙3. *Preparation of the colloidal crystal template and infiltration with PDMS*. – The composite structure based on PS NPs embedded in the PDMS matrix was obtained as reported in fig. 1. The colloidal crystal was assembled into a 3D structure on a PET sheet using the VD technique as shown in fig. 1(a). As a first step the substrate was hydrophilized using an ozone cleaner for 30 min. Then, the clean PET sheet was immersed in the PS NPs suspension and the cylindrical vessel placed in a homemade PID oven at controlled temperature of 45 °C for 48 h to form a film (fig. 1(a)). The infiltration with PDMS was obtained by pouring the fluid solution into the voids of the colloidal crystal. The elastomer was supplied as a kit with two separate components: base and curing agent; to be mixed in 10:1 ratio. After infiltration the structure was thermally cured for 4 h at 65 °C and the excess elastomer was peeled-off from the surface.

2˙4. *Characterization*. – The morphology and size of both PS NPs and colloidal crystal were investigated using atomic force microscopy (AFM NT-MDT P47H). The optical
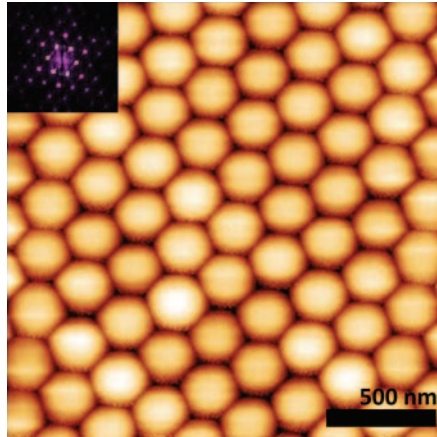
Fig. 2. – AFM image of the top surface of the PS NPs colloidal crystal formed by VD. The inset displays the FFT of the AFM image.

properties of the colloidal crystals were characterized using a miniature UV-VIS reflection fiber optic spectrometer (Ocean Optics USB 200) equipped with a halogen lamp. The incident light was aligned perpendicular to the $\langle 111 \rangle$ planes of the colloidal crystal. UV-VIS spectra were collected under perpendicular irradiation of white light. Dynamic spectra were continuously recorded by Ocean Optics USB 200 spectrometer coupled to a six-around one reflection probe with incident and reflection angles fixed at $0\,°$ (fig. 1(c)). The reflection spectra were collected every $2\,\mathrm{sec}$ after spotting $200\,\mu l$ of the chosen solvent on the surface of the colloidal crystal. In $5\,\mathrm{min}$ about 300 spectra were imported to the matrix table of software OriginPro, which was further used to plot the contour map with time (t) in x-axis, reflection frequency (THz) in y-axis and reflection intensity (R) in color.

3. – Results and discussion

The VD technique allows obtaining high quality periodic dielectric monodisperse polystyrene spheres assembly [37]. In fact, as shown in fig. 2, a well-ordered close packed structure, that can be attributed to planes $\langle 111 \rangle$ of a face centred cubic (fcc) system [38] is evident. Moreover, the presence of long-range crystalline order, can be confirmed by the sharp spots of Fast Fourier Transforms (FFT) image, calculated from fig. 2 and reported in the inset.

As described in the experimental section, the direct colloidal crystal was fully infiltrated with a specific responsive material such as PDMS that is one of the most widely used silicon-based elastomers, since it presents a low glass transition temperature, high transmittance and, last but not least, can be swelled by some organic solvents [39]. Initially we have demonstrated that this structure can be used as a chemical sensor, in fact we have verified that the system presents a different response as a function of the organic solvent dropped on its surface (see fig. 3). In the specific we used the following chemicals: EG, EtOH, tert-BuOH, MeOH, 1cSt and 10cSt silicon fluid, because they present different capability to swell the elastomeric matrix as reported by Lee [39].

In this paper, in order to assess the chromatic behavior of the composite structure
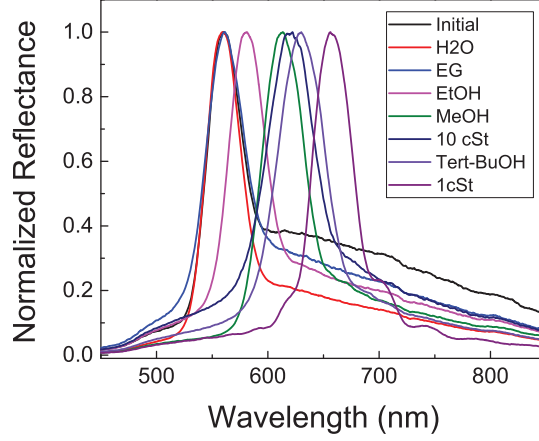
Fig. 3. – Black line corresponds to the reflectance of the polymeric composite system. Reflectance spectra were acquired after spotting $2\,\mu l$ of different solvents onto the "sensor" surface, and monitoring the optical change of the diffraction peak. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

and therefore its variation in the optical response under external stimuli, an analytical model based on the Bragg's law is proposed. Its worth recalling that the opalescence and, therefore, the reflectance wavelength for normal incidence, can be predicted by eq. (1)

$$(1) \qquad \frac{c}{\nu} = 2d_{111}n_{eff},$$

where ν is the peak frequency of reflected light, d_{111} is the interlayer spacing ($= 0.816D$ in the initial configuration) in the $\langle 111 \rangle$ direction, D represents the diameter of PS NPs and n_{eff} is the effective refractive index of the sample. In a two-phase structure the effective refractive index can be estimated by eq. (2)

$$(2) \qquad n^2_{eff} = n^2_{spheres}f_i + n^2_{medium}(1 - f_i),$$

where, in the initial state, $f_i = 0.74$ is the filling factor of the porous structure for an ideal fcc package and $n_{spheres} = 1.55$ and $n_{medium} = 1.40$ represent the refractive index, at $632\,\mathrm{nm}$, of PS and PDMS materials, respectively. Furthermore, the width of bandgap $\Delta\nu$, normalized to the bandgap frequency ν, depends on the materials chosen and can be expressed by eq. (3),

$$(3) \qquad \frac{\Delta\nu}{\nu} \approx \left| \frac{n_{spheres} - n_{medium}}{n_{eff}} \right|,$$

where $\frac{\Delta\nu}{\nu}$ is roughly proportional to refractive index contrast between particles and matrix normalized to the effective refractive index [40].

The application of an external stimulus, in our case the solvent spotted on the composite surface, produces a specific change in the lattice constant value a_i ($a_i = (d_{111})_i\sqrt{3}$)
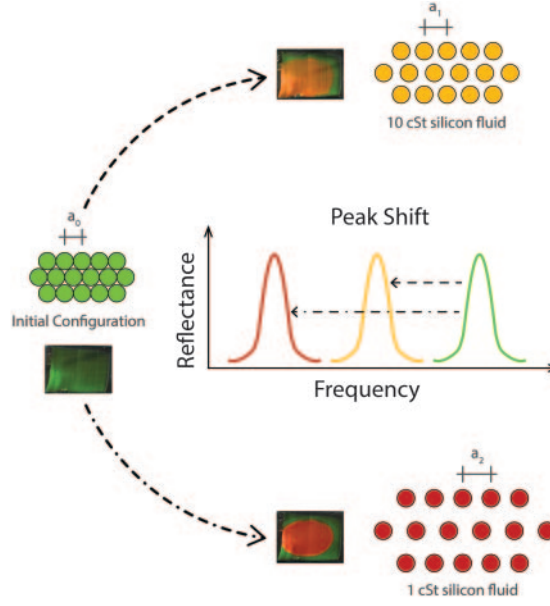
Fig. 4. – Sketch of the working principle of the composite structure as a function of the applied solvent: (green color) initial state, (orange color) 10cSt silicon fluid, (red color) 1cSt silicon fluid, with their respective reflectance peak shift.

and accordingly in the filling factor f_i, as expressed by eq. (4)

$$(4) \qquad f_i = \frac{2\pi}{3} \frac{D^3}{a_i^3},$$

where D is the dimension of the nanoparticles. Since the external stimulus is responsible of a modification in the volume fraction of the PS NPs in the crystal as sketched in fig. 4, the application of the solvent results in a new value of f_i that induces a blue shift in the optical response as expressed by eq. (1). We can consider, in the simplest case, an isotropic displacement of the spheres assembled in the periodic lattice fcc (fig. 4), that causes a variation in the value of the effective refractive index n_{eff} as well as on the d_{111}.

This assumption has been confirmed through the determination of the swelling coefficient S and its comparison with the tabulated data. S is defined by eq. (5)

$$(5) \qquad S = \frac{(d_{111})_s}{(d_{111})_0},$$

where $(d_{111})_{s,0}$ is the interplanar spacing in the presence of the solvent (swelled state) and for initial configuration (initial state), respectively. The values calculated for specific solvents (MeOH and tert-BuOH), compared with tabulated ones, are reported in table I.

From the data of table I an optimum agreement is evident confirming that the model based on Bragg's law and on the assumption of an isotropic displacement of the nanospheres is proper to describe the working principle of the colloidal structure.

As previously mentioned, the composite structure can be usefully employed as a chemical sensor based on the change in the filling factor f_i that causes a variation in

TABLE I. – *Swelling coefficient S of the solvent used to validate the model, an error of 5% is attributed to the measured values.*

analyte	Swelling coefficient S	
	S tabulated [39]	S calculated
MeOH	1.02	1.03
tert-BuOH	1.21	1.19

the photonic band gap features like frequency position of the reflectance peak and its broadening. On this base the colloidal crystal has been exploited in order to analyze tert-BuOH/water mixtures by means of static and dynamic reflectance measurements. In our case we have performed static and dynamic measurements in order to analyze and discriminate between different mixtures of tert-BuOH and water, taking advantage of the capability of the mixtures to diffuse differently and swell PDMS with singular kinetics. Using the static approach, $2\,\mu l$ of various concentrations of tert-BuOH and water were spotted on the surface of the composite colloidal crystal. Figure 5 shows the reflectance peak shift referred to compositions ranging from pure water to pure tert-BuOH. Since the PDMS hardly swells in pure water, the peak shift was very small due to the hydrophobic condition. In this system there is a little peak shift up to approximately 90 vol. % of tert-BuOH concentration, as evidenced in fig. 5. Above this concentration (PDMS elastomer swollen mostly with tert-BuOH and a small amount of water), the slope of the line changes abruptly.

In fact, we can distinguish two main regions, the first one goes from 0% to 90% of tert-BuOH, in which only a moderate decrease in term of frequency (22 THz) is observable, while in the second one, that goes from 90% to 100%, there is a much steeper slope with a variation of 30 THz. The non-ideal solution behaviour of this PDMS-solvent system can find an explanation if we consider that the value of the solubility parameter for a
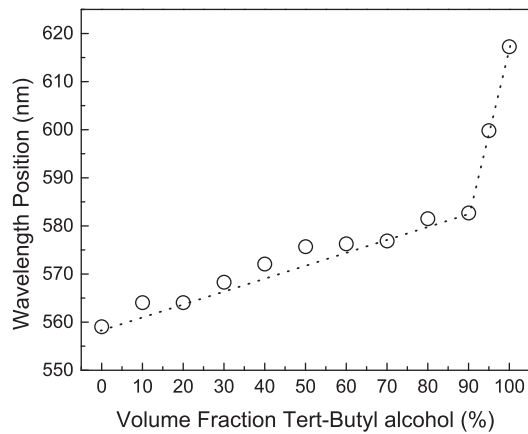

Fig. 5. – Relationship between red shift of the reflectance spectra and the tert-BuOH concentration.
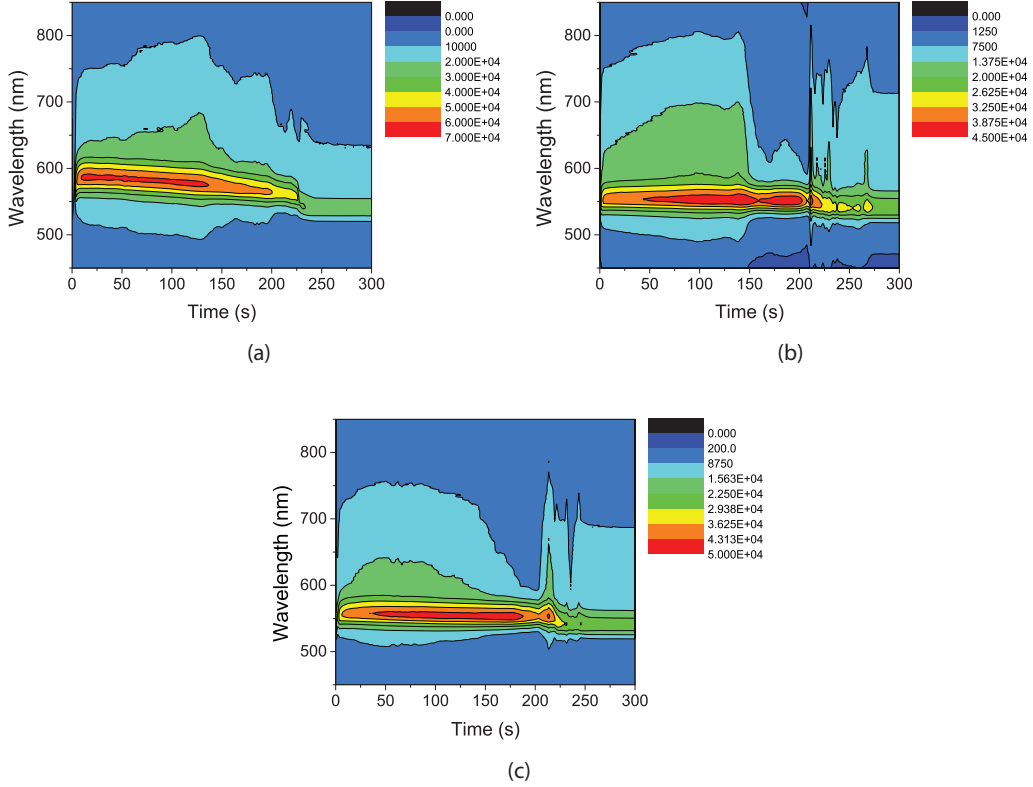
Fig. 6. – Dynamic Reflectance patterns of the (a) pure tert-BuOH, (b) 95% tert-BuOH− 5% H_2O mixture and (c) 90% tert-BuOH− 10% H_2O mixture.

solvent mixture is hardly ever volume-wise proportional to the solubility parameters of the two components [41].

A complementary approach based on dynamic measurements in order to discriminate volatile organic compounds and homologues has already been applied by Lova *et al.* [30] and Ge *et al.* [32], respectively. Here we want to exploit this kind of measurements to follow different processes happening when the solvent mixture is applied on the surface of the composite. The continuous variation of the observed pattern is reported in fig. 6, where the horizontal axis represents time (s), the vertical one represents frequency (THz) and the colours give the measured reflectance intensity.

Analyzing fig. 6 we can observe a variation in the dynamic spectra due to the singular capability of the mixtures to diffuse into the structure and evaporate with different kinetics depending on their polarity, viscosity and chemical affinity. This produces a sort of finger print pattern that permit an easy, fast and precise discrimination among different mixtures.

4. – Conclusions

An easy and reliable method for the fabrication of composite colloidal crystals based on PS nanoparticles embedded in an elastomeric matrix has been developed. We have proved that these systems can be employed as low cost and reversible chromatic sensors

for the investigation of solvents and mixtures. In addition, we have investigated the working principle of this class of sensors, assessing the crucial role that the filling factor f plays both in the position of the diffraction peak and in its broadening. It has been demonstrated that the developed structures and the static and dynamic reflectance measurements permit to selectively distinguish among different solvents and mixtures even in small concentration. Finally, the prepared structure and the interrogation approach, which does not require any signal transduction, can be seen as a suitable tool for the development of a safe device also suitable for untrained end-users.

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REFERENCES

[1] YABLONOVITCH E., *Phys. Rev. Lett.*, **58** (1987) 2059.
[2] JOHN S., *Phys. Rev. Lett.*, **58** (1987) 2486.
[3] LOPEZ C., *Adv. Mater.*, **15** (2003) 1679.
[4] CHIAPPINI A., ARMELLINI C., CHIASERA A., FERRARI M., JESTIN Y., MATTARELLI M., MONTAGNA M., MOSER E., NUNZI CONTI G., PELLI S., RIGHINI G. C., CLARA GONCALVES M. and ALMEIDA RUI M., *J. Non-Cryst. Solids*, **353** (2007) 674.
[5] LIN S. Y., FLEMING J. G., HETHERINGTON D. L., SMITH B. K., BISWAS R., HO K. M., SIGALAS M. M., ZUBRZYCKI W., KURTZ S. R. and BUR J., *Nature*, **394** (1998) 251.
[6] NODA S., TOMODA K., YAMAMOTO N. and CHUTINAN A., *Science*, **289** (2000) 604.
[7] SUN H.B., MATSUO S. and MISAWA H., *Appl. Phys. Lett.*, **74** (1999) 786.
[8] DEUBEL M., VON FREYMANN G., WEGENER M., PEREIRA S., BUSCH K. and SOUKOULIS C. M., *Nat. Mater.*, **3** (2004) 444.
[9] COLVIN V. L., *Mater. Res. Soc. Bull.*, **26** (2001) 637.
[10] FUDOUZI H. and XIA Y., *Adv. Mater.*, **15** (2003) 892.
[11] RECULUSA S. and RAVAINE S., *Chem. Mater.*, **15** (2003) 598.
[12] BARDYSHEV I. I., MOKRUSHIN A. D., PRIBYLOV A. A., SAMAROV E. N., MASALOV V. M., KARPOV I. A. and EMELCHENKO G. A., *Colloid J.*, **68** (2006) 20.
[13] JETHMALANI J. M., SUNKARA H. B., FORD W. T., WILLOUGHBY S. L. and ACKERSON B. J., *Langmuir*, **13** (1997) 2633.
[14] JIANG P., BERTONE J. F., HWANG K. S. and COLVIN V. L., *Chem. Mater.*, **11** (1999) 2132.
[15] HOLGADO M., GARCÍA-SANTAMARÍA F., BLANCO A., IBISATE M., CINTAS A., MÍGUEZ H., SERNA C. J., MOLPECERES C., REQUENA J., MIFSUD A., MESEGUER F. and LPEZ C., *Langmuir*, **15** (1999) 4701.
[16] GALISTEO-LPEZ J. F., IBISATE M., SAPIENZA R., FROUFE L., BLANCO A. and LOPEZ C., *Adv. Mater.*, **23** (2011) 30.
[17] AGUIRRE C. I., REGUERA E. and STEIN A., *Adv. Funct. Mater.*, **20** (2010) 2565.
[18] LI H., CHANG L., WANG J., YANG L. and SONG Y., *J. Mater. Chem.*, **18** (2008) 5098.
[19] BURGESS I. B., MISHCHENKO L., HATTON B. D., KOLLE M., LON M. and AIZENBERG J., *J. Am. Chem. Soc.*, **133** (2011) 12430.
[20] CHIAPPELLI M. C. and HAYWARD R. C., *Adv. Mater.*, **24** (2012) 6100.
[21] CHEN M., ZHANG Y. P., JIA S. Y., ZHOU L., GUAN Y. and ZHANG Y. J., *Angew. Chem. Int. Ed.*, **54** (2015) 9257.
[22] ZHANG J. T., WANG L. L., LUO J., TIKHONOV A., KORNIENKO N. and ASHER S. A., *J. Am. Chem. Soc.*, **133** (2011) 9152.

[23] Colusso E., Perotto G., Wang Y., Sturaro M., Omenetto F. and Martucci A., *J. Mater. Chem. C*, **5** (2017) 3924.

[24] Fudouzi H. and Sawada T., *Langmuir*, **22** (2006) 1365.

[25] Arsenault A. C., Puzzo D. P., Manners I. and Ozin G. A., *Nat. Photonics*, **1** (2007) 468.

[26] Shieh J. Y., Kuo J. Y., Weng H. and Yu H. H., *Langmuir*, **29** (2013) 667.

[27] Ding T., Smoukov S. K. and Baumberg Jeremy J., *Nanoscale*, **7** (2015) 1857.

[28] Liu J., Zhang Y., Zhou R. and Gao L., *J. Mater. Chem. C*, **5** (2017) 6071.

[29] Xiao F., Li G., Wu Y., Chen Q., Wu Z. and Yu R., *Anal. Chem.*, **88** (2016) 9207.

[30] Lova P., Bastianini C., Giusto P., Patrini M., Rizzo P., Guerra G., Iodice M., Soci C. and Comoretto D., *ACS Appl. Mater. Interfaces*, **8** (2016) 31941.

[31] Kuo W. K., Weng H. P., Hsu J. J. and Yu H. H., *Appl. Sci.*, **6** (2016) 67.

[32] Zhang Y., Fu Q. and Ge J., *Nat. Comm.*, **6** (2015) 7510.

[33] Xiong C., Zhao J., Wang L., Geng H., Xu H. and Li Y., *Mater. Horizons*, **4** (2017) 862.

[34] Zhang Y., Qiu J., Hu R., Li P., Gao L., Heng L., Tang B. Z. and Jiang L., *Phys. Chem. Chem. Phys.*, **17** (2015) 9651.

[35] Daoussi R., Vessot S., Andrieu J. and Monnier O., *Chem. Eng. Res. Des.*, **87** (2009) 899.

[36] Vessot S. and Andrieu J., *Drying Technol.*, **30** (2012) 377.

[37] Chiappini A., Armellini C., Chiasera A., Ferrari M., Fortes L., Clara Gonalves M., Guider R., Jestin Y., Retoux R., Nunzi Conti G., Pelli S., Almeida Rui M. and Righini G. C., *J. Non-Cryst. Solids*, **355** (2009) 1167.

[38] Miguez H., Lopez C., Meseguer F., Blanco A., Vazquez L., Mayoral R., Ocana M., Fornes V. and Mitsud A., *Appl. Phys. Lett.*, **9** (1997) 1148.

[39] Lee J. N., Park C. and Whitesides G. M., *Anal. Chem.*, **75** (2003) 6544.

[40] Shkunov M. N., Vardeny Z. V., DeLong M. C., Polson R. C., Zakhidov A. A. and Baughman R. H., *Adv. Funct. Mat.*, **12** (2002) 21.

[41] Barton A., *Chem. Rev.*, **75** (1975) 731.