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Hybrid ZnO:polystyrene nanocomposite for all-polymer photonic crystals

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We report on ZnO nanoparticles-polystyrene (PS) nanocomposites (NC) engineered to modify PS matrix permeability and refractive index (n), and to fabricate 1D all-polymer photonic crystals (PC) for sensing applications. The new NC can be easily processed from solutions to prepare high quality thin films by spin coating. ZnO nanoparticles (n=1.98) have been synthetized by solvothermal route and grafted with a silane to reduce phase segregation in the PS matrix (n=1.58). Such procedure led to an increase of the matrix refractive index of about 1%. By casting alternated layers of the NC and cellulose acetate (CA, n=1.46), we fabricated free-standing and flexible distributed Bragg reflectors (DBRs) of excellent optical quality. Preliminary results on the use of such DBRs as solvent vapor sensors are reported.

1 Introduction

PCs, i.e. sub-micrometric lattices of materials having different refractive index, are nowadays widely used to empower sensors [1-3], waveguides [4-6], photovoltaic devices [7-9], displays [10, 11] and control spontaneous emission and lasing [12-15]. PCs of different dimensionality can be prepared by either top-down or bottom-up methods [16, 17]. In this regard, 1D multilayers made by alternated semiconductors or metal oxides have been studied for more than 30 years due to their straightforward structure [18]. Although these lattices are very simple, their fabrication can be time and energy demanding. As a consequence, all-polymer DBRs are arising increasing attention due to their mechanical flexibility, low cost and rapid fabrication methods such as self-assembly [19-21], coextrusion [22] and spin-coating [23, 24].

However, when photonic crystals are used as sensors, the low permeability characteristic of non-crystalline polymers represents a challenge. Photonic crystals sensors are generally based on the modification of refractive index or lattice periodicity due to molecules penetration into the structure [25, 26]. Notwithstanding the penetration of liquid analytes into 1D polymer lattices can produce a strong variation of such parameters, gas and vapor sensing presents some issues. As a matter of fact, this process is widely exploited by highly porous 3D PCs [26-29] but, sophisticated optical geometries are necessary when polymer DBRs are the object of interest [30-33].

Unfortunately, the production of vapor responsive PCs may be costly from both economical and time point of views. For this reason, inorganic and hybrid 1D photonic structures are nowadays widely investigated [34, 35] for the fabrication of fast responsive sensors [36-41] besides optical coatings [42], displays [11], photovoltaic devices [43] and lasers [44]. These materials are usually prepared by spin coating of colloidal nanoparticles suspensions which are then annealed to sinter the particles and to provide structure stability. These structures can also be embedded into a flexible structural matrix allowing free-standing DBRs [45-47].

Polymer DBRs have also been proven to be suitable for vapors sensing. Convertino *et al.* demonstrated an acetone vapor responsive DBR made by bare and gold doped polytetrafluoroethylene grown by chemical vapor deposition [48]. In 2006, Mönch *et al.* reported on DBRs made by spin coating and *in situ* polymerization of poly(methyl methacrylate) e PS monomeric precursors. Such systems have been shown to be sensitive to toluene and acetone vapors [49].

Polymer DBRs prepared by spin coating present the advantages of faster production and lower costs. On the other hand, the low porosity typical of polymers and the relatively low available dielectric contrast are challenging issues. The spin coating technique requires in fact the use orthogonal solvents thus limiting the suitable materials [13]. To achieve good vapor response, a nanofiller can be loaded into a polymer film modifying its sub-nanometric porosity and increasing its permeability [50-52]. This process will also affect the matrix refractive index, which is obtained as the volume weighted average of the dielectric function of the components (effective medium) [48, 53]. The opportunity to increase the dielectric contrast (with respect to well-known cases [13, 23]) joined to the permeability promises might open new perspectives in the use of polymer nanocomposites in PC sensing applications. In this work, we report on the preparation of highly ordered multilayers made by CA and PS where the latter is doped with ZnO nanoparticles (NPs). NPs were prepared by solvothermal synthesis and engineered to increase PS permeability and refractive index. Flexible and free-standing photonic structures are investigated (Fig. 1). Optical characterization for such 1D PC and their possible uses as a platform for sensing applications are reported.

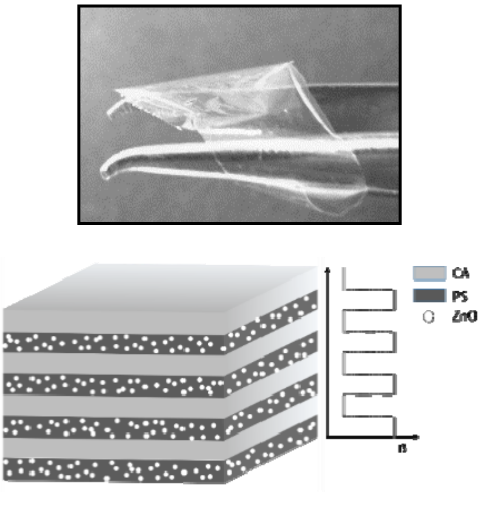

Figure 1 Photograph and scheme of a free standing polymer DBR.

2 Experimental procedures

ZnO NPs were synthetized via a solvothermal route. In a typical process, a methanol solution of KOH and zinc acetate is heated at 63 °C and sonicated for 3 h. The NPs are then purified by five cycles of decantation and washing with methanol and finally dried [54]. To avoid particles aggregation in the PS matrix, dimethylmethoxy-octadecylsilane (DMOS) was grafted onto the NPs surface. To gather the grafting, 10 g of NPs and 2.5 g of DMOS were sonicated in a solution of methanol and dichloromethane until complete evaporation and desiccated in a vacuum. The graft reaction was performed at 135°C under N_2 flux for 2 h [55, 56]. The grafted NPs were then suspended in a toluene solution of PS (M_w=200000) and stirred for more than 36 h. DBRs of alternated layers of NC and a CA (M_w=61000) in diacetonalcohol were grown by dynamic spin-coating using polymer concentration ranging from 3% to 5% (v/v) and a rotation speed of 6000 revolutions per minute [13].

ZnO NPs were analyzed by scanning electron microscopy (SEM) using a field emission FEI Inspect FTM microscope. NPs crystal structure was identified by X-Ray Diffraction (XRD) with a Bragg-Brentano goniometer Philips PW1830. The complex refractive index (n+ik) of bare polymer films was determined by spectroscopic ellipsometry (SOPRA ES4G). A first rough evaluation of the refractive index of the nanocomposite has been obtained by using the Maxwell-Garnett effective medium theory [13, 32, 57]. Reflectance and transmittance spectroscopy was performed using optical setups based on optical fiber coupled Avantes 2048 spectrometers (200–1100 nm, resolution 1.4 nm) and on Arcoptics FT-interferometer (900-2600 nm, resolution 8 cm^{-1}). The light source was a combined deuterium–halogen lamp Micropak DH2000BAL. For the evaluation of the DBR response to vapor exposure, samples were inserted in a closed cuvette connected to a solvent reservoir where spontaneous solvent evaporation occurs at room temperature (about 25°C). The cuvette was then inserted in a standard cuvette holder with optical fiber connectors. Transmittance measurements were recorded for about 20 minutes during solvent spontaneous evaporation every 5 minutes.

3 Results and discussion

SEM image of Fig. 2a shows ZnO NPs having an average size of 24 nm. Such size is small enough to reduce light scattering effects, which are detrimental for the photonic structure.

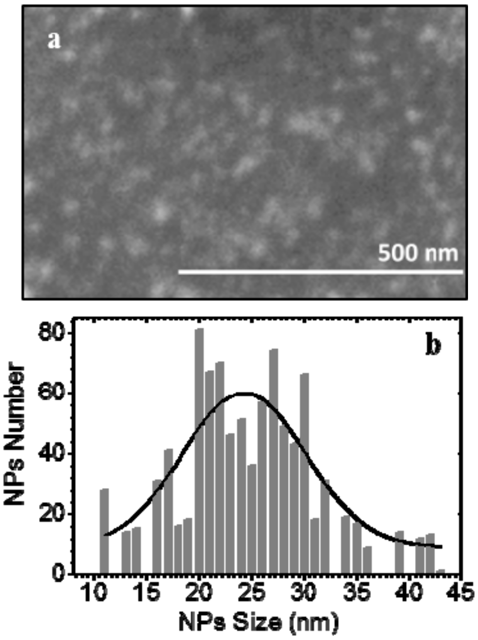

Figure 2 (a) SEM micrograph of ZnO NPs. (b) Distribution of ZnO NPs diameters.

The NPs XRD pattern displayed in Fig. 3 can be indexed to ZnO wurtzite [58] with maximum intensities at 2θ angles: 31.8, 34.6, 36.11, 47.6, 56.5 and 63.0. Peaks half width at half maximum was related to the crystal dimension [59] obtaining an average size of 25 nm, in agreement with the SEM data reported in Fig. 2.

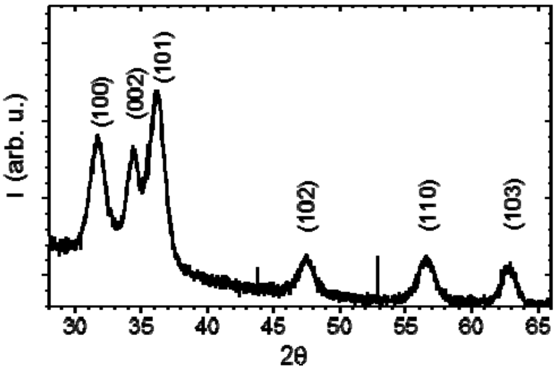

Figure 3 ZnO NP XRD pattern.

After the grafting process, NPs were added to a PS solution in toluene for thin films and DBRs preparation. Preliminary results on the complex refractive index of both PS and NC are reported in Fig. 4. The bare PS extinction coefficient (k) is negligible over the whole spectral range and its refractive index shows the well-known dispersion with values in agreement with literature data [13, 60]. The n and k spectra of NC thin films loaded with 2.5% (v/v) of ZnO NPs were calculated by the effective medium model [57] using literature data [61] for crystalline ZnO and compared with those of bare PS. The NC k spectrum shows a clear absorption peak below 400 nm, with a correspondent counterpart in the n spectrum [61]. These well-defined peaks are not observed in ellipsometric measurements, which anyway account for broader structures in the same spectral range of comparable intensity. The behavior of n spectrum is instead very well fitted by the ellipsometric data and exhibits a clear increase of about 1% with respect to bare PS (Fig. 4).

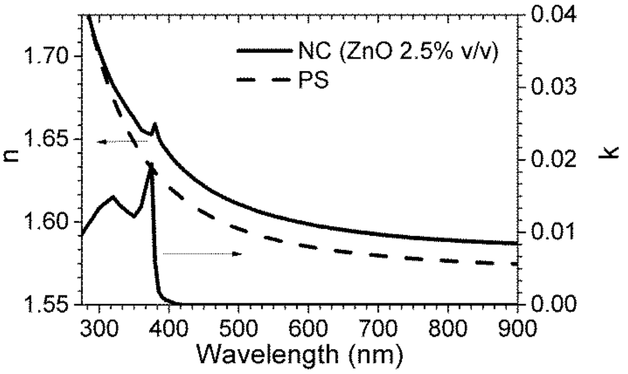

Figure 4 PS and NC complex refractive index dispersion.

NC (ZnO 2.5% v/v_{PS}) and CA solutions were then used to prepare a 15 bilayers DBR whose reflectance spectrum is reported in Fig. 5. The spectrum is characterized by peaks at 1505 nm, 758 nm, 506 nm and 386 nm which are assigned to the first order photonic band gap (PBG) followed by higher diffraction orders. Moreover, the reflectance spectrum baseline shows interference fringes pattern due to the overall thickness of the DBR. All such findings testify the good processability of the NC and the excellent optical quality of the DBR.

In the same figure, the theoretical spectrum calculated by the transfer matrix methods is reported. The very good agreement between theory and experiments points out once more the quality of the structures prepared using the NC as high refractive index material.

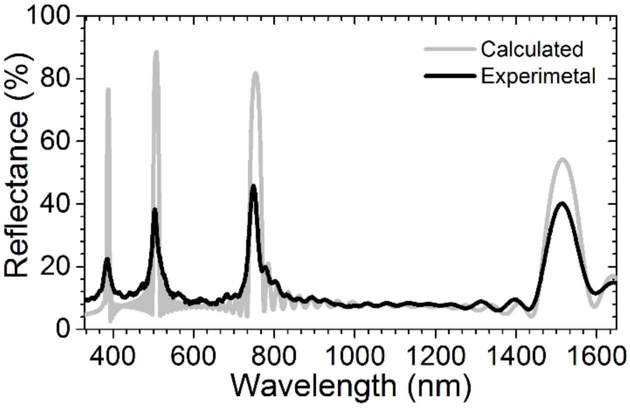

Figure 5 Experimental and calculated reflectance spectra of a CA:NC DBR made by 15 bilayers.

DBRs were finally exposed to toluene vapors in a sealed cuvette connected to a toluene reservoir where spontaneous evaporation occurs. Figure 6 compares the spectral variation of the PBG for a PS:CA (Fig. 6a) and NC:CA (Fig. 6b) DBRs. Spectra are reported as transmittance contour plots to better highlight PBG variations upon solvent vapor exposure.

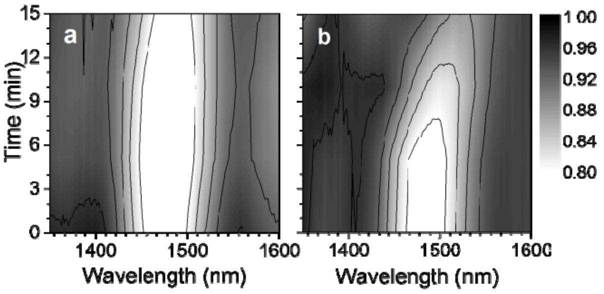

Figure 6 Contour plots showing the transmittance spectra of (a) PS:CA and (b) NC:CA DBRs exposed to toluene vapors.

For PS:CA DBR, minor spectral changes are observed within the first fifteen minutes of exposure (Fig. 6a). For NC:CA DBR, a remarkable change of 50 nm is observed using the same exposure conditions (Fig. 6b). Similar effects occur for the higher order PBGs. Such impressive differences in the spectral response of the two structures may be due to PS swelling after exposure to non-polar solvent [62]. The much stronger effect observed for the NC: CA DBR seems to be due to the increased permeability of NC (with respect to bare PS) probably driven by the disorder and porosity induced by the ZnO NPs. The low response of standard PS:CS DBR should not instead surprise being PS widely used for packaging thanks to its low permeability to gas and vapors [52].

4 Conclusions

A novel solution processable ZnO:PS NC possessing a refractive index increased up to 1% with respect to PS has been prepared. The new NC allows to grow excellent optical quality DBR showing up to the 4th order of diffraction for the PBG. Such DBRs have shown an increased response than those grown by bare PS to toluene vapors thus opening new perspectives into color responsive all-polymer PC sensors.

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