Electronic Supplementary Information

# Ultrafast Assembly of Nanoparticles to Form Smart Polymeric Photonic Crystal Film: A New Platform for Quick Detection of Solution Compositions

*Xiuqing Shen, Pan Wu, Christian G. Schäfer and Changchun Wang**

State Key Laboratory of Molecular Engineering of Polymers, Department of Macromolecular Science, and Laboratory of Advanced Materials, Fudan University, 220 Handan Road, Shanghai 200433, China

*To whom correspondence should be addressed. E-mail: ccwang@fudan.edu.cn

**Materials**

Styrene (St), ethyl acrylate (EA), sodium dodecylsulfate (SDS), sodium persulfate, n-octane, ethanol were purchased from Sinopharm Chemical Reagent (Shanghai, China). Butanediol diacrylate (BDDA) was purchased from TCI (Shanghai). Allyl methacrylate (AMA) was obtained from Acros Organics USA. Potassium hydroxide (KOH), diethylene glycol dimethacrylate (DEGDMA), benzophenone, 2-hydroxy-2-methylpropiophenone and aluminium oxide were obtained from Aladdin (Shanghai, China). Dowfax2A1 was purchased from Dow Chemicals. Diethylene glycol methyl ether methacrylate (DEGMEMA) was obtained from Sigma-Aldrich (Shanghai). Before emulsion polymerization, purification process was carried out in order to remove stabilizers in monomers. EA was treated sequentially with 1 M sodium hydroxide solution, water for a neutral state and sodium sulfate for water extraction. DEGMEMA and St were purified by an alumina (basic, 200-300 mesh) column. All the other chemicals were used as received if not mentioned. Polyethylene terephthalate (PET) films were purchased from Shantou Ruixin Thin Film Technology Co. Ltd. (Dongxin, TD60-125U). Deionised water was used in all our experiments.

**Calculation of thickness of the PC film according to thin film interference**

Thin-film interference is a phenomenon that the light reflected by the upper boundary and the light reflected by the lower boundary interfere with one another, resulting in either enhancement or reduction of light intensity.

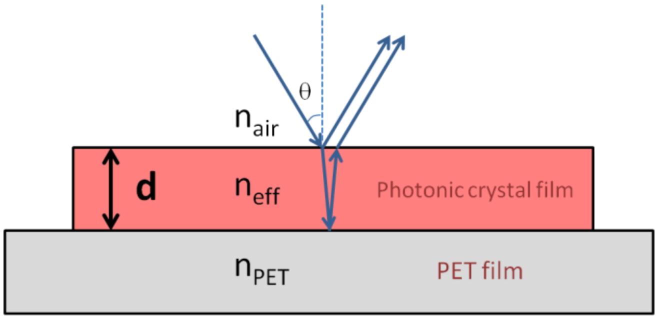


**Figure S1.** Schematic illustration of thin-film interference. Light reflected by the lower and upper boundaries interfere with one another.

The relationship between refractive indexes of air, PC film and PET film is as follows:

$$n_{air} < n_{eff} < n_{PET}, \qquad (1)$$

According to thin-film interference theory, under the condition of normal incidence (θ = 0°), when the reflected lights reinforce each other and the intensity reaches the maximum, the relationship between thickness of the film (d) and wavelength of light is expected to be:

$$2d \cdot n_{eff} = i \cdot \lambda_i, \qquad (2)$$

Where i is an integer, $\lambda_i$ is the wavelength of the $i_{th}$ crest, $n_{eff}$ is the effective refractive index of the PC and d is the thickness of the PC film. Half-wave loss is taken into consideration.

$$2d \cdot n_{eff} \cdot \lambda_i^{-1} = i, \qquad (3)$$

According to the data of the reflection spectra, when intensity reaches maximum value, the corresponding wavelength was recorded as $\lambda_i$.

$$2d \cdot n_{eff} \cdot \left(\lambda_i^{-1} - \lambda_{i+5}^{-1}\right) = 5, \qquad (4)$$

5 cycles are included for 1 series of calculation for improvement of accuracy.

$$d = 5(2n_{eff}({\lambda_i}^{-1} - {\lambda_{i+5}}^{-1}))^{-1}, \quad (5)$$

The calculation was repeated for 6 times.

**Characterization of the refractive index contrast of the matrix in which PS cores embedded**

The core of the particle is polystyrene with a higher refractive index of 1.58. After UV curing, the matrix in which the PS cores embedded is copolymer mainly consisting of 17% PEA and 83% PDEGMEMA. The refractive index of PDEGMEMA is 1.456 which was measured by an Abbe refractometer (25 °C, Shanghai Shenguang Instrument Co., Ltd., WAY-2S). The mean effective refractive index of the matrix is 1.46 calculated according to Equation (1):

$$ {n_{eff}}^2 = {n_p}^2 V_p + {n_m}^2 V_m \quad (1)$$

$V_p$ and $V_m$ are the respective volume fractions.[1, 2] Therefore, the contrast of the refractive index between the PS cores and the matrix is 0.12.

**Table S1.** Hydrodynamic diameters of the monodisperse particles after each step of stepwise emulsion polymerization collected by DLS measurements.

| Sample | $d_{\text{purple}}$ (nm) | $d_{\text{green}}$ (nm) | $d_{\text{red}}$ (nm) |
|---|---|---|---|
| Seed | 42 ± 1 | 55 ±1 | 56 ± 1 |
| Core | 139 ± 1 | 183 ± 3 | 197 ± 1 |
| Core-interlayer | 141 ± 2 | 197 ± 1 | 215 ± 1 |
| Core-interlayer-shell | 174 ± 2 | 225 ± 1 | 240 ± 1 |

$d_{\text{purple}}$, $d_{\text{green}}$ and $d_{\text{red}}$ are hydrodynamic diameters for particles forming PC films with purple, green and red colors at θ = 0°, respectively.


**Figure S2**. Images of the PC film under different angles of incident light (0°, 10°, 20°, 30°, 50°)

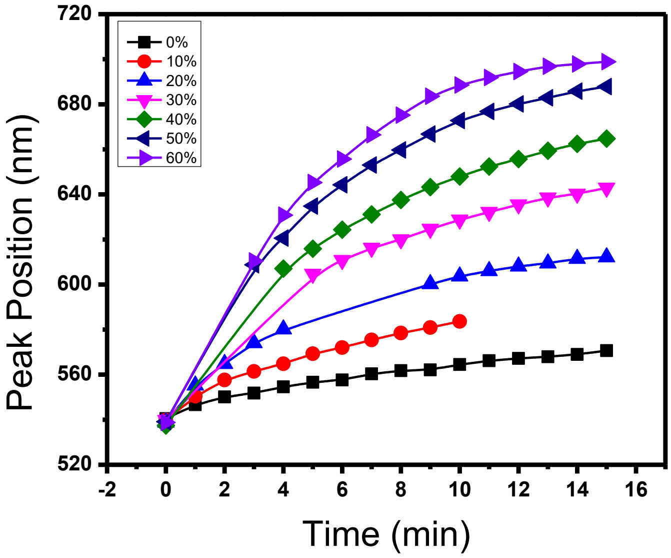


**Figure S3.** Correlation of the peak position of the reflection spectra and the response time with different ethanol concentrations which were detected by fiber optic sensor.

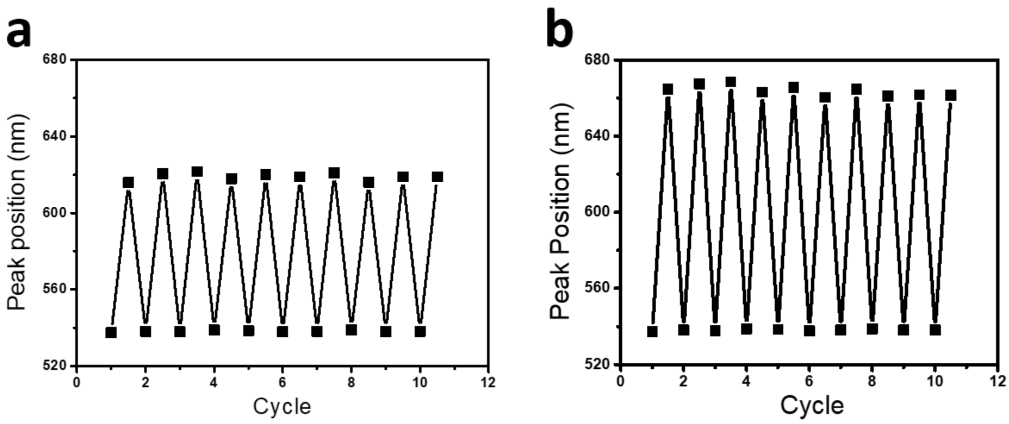


**Figure S4**. Reproducible ethanol/water vapor sensing with response time of a) 5 min and b) 15 min of the fiber optic sensor. The ethanol vapor sensor is fully reversible with different response time.

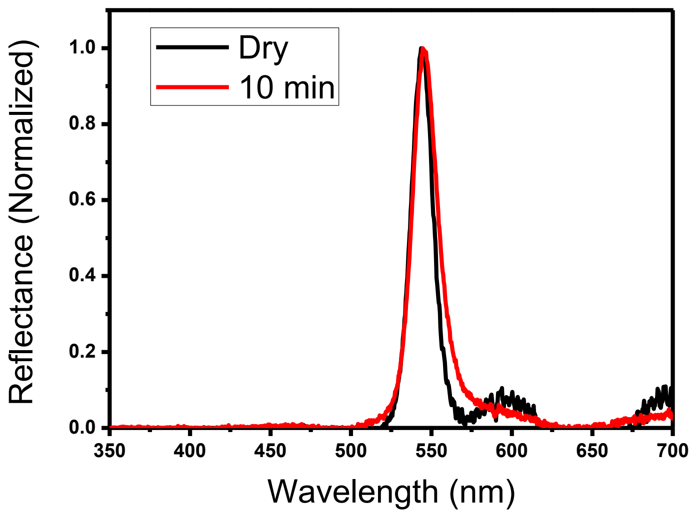


**Figure S5.** Reflection spectra of the PC film at normal incidence before and after being immersed in pure *n*-octane for 10 min.

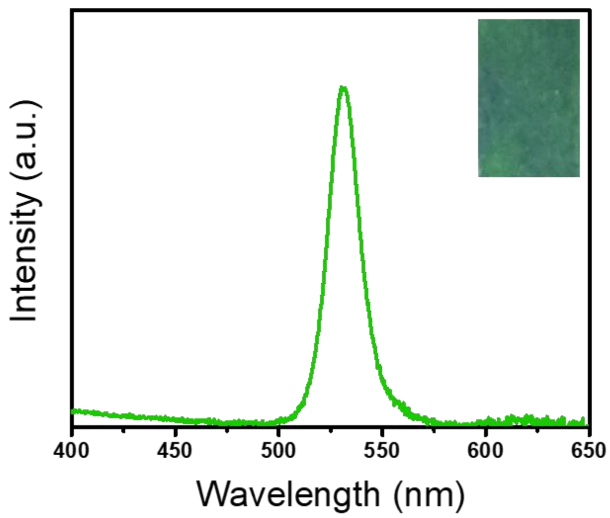


**Figure S6.** Reflection spectra and picture of the PC film which was consisted of PS particles and styrene. The mass fraction of PS particles is 45%.

REFERENCE:

1. Y.-J. Lee and P. V. Braun, *Adv. Mater.,* 2003, **15**, 563.

2. C. Fenzl, T. Hirsch and O. S. Wolfbeis, *Angew. Chem. Int. Ed.,* 2014, **53**, 3318.