Electronic Supplementary Information

Direct-Writing Colloidal Photonic Crystal Microfluidic Chips by Inkjet Printing for Label-Free Protein Detection

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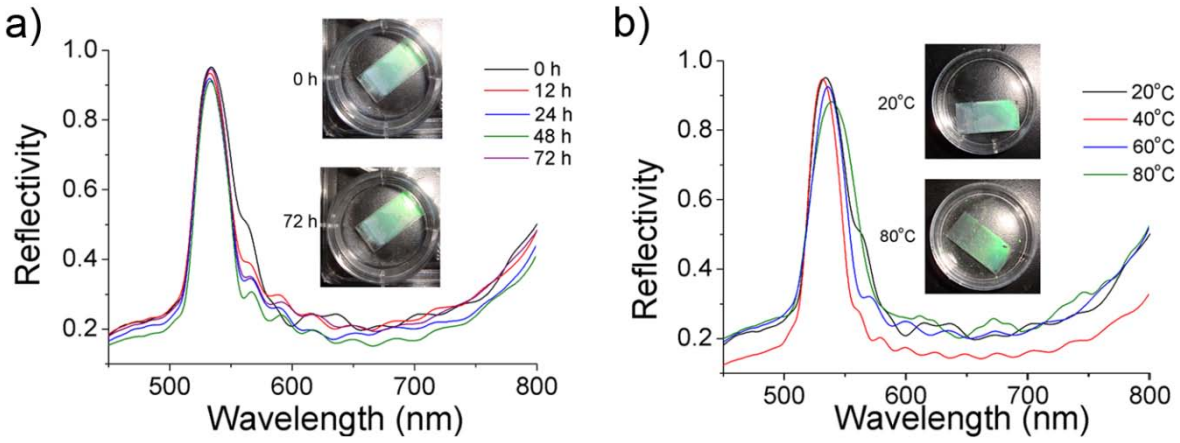

Fig. S1 The durability of the colloidal PC in the water. a) The colloidal PC can resist 72 h soaking in the water at the room temperature. b) The colloidal PC can resist 80˚C heating in the water for 2 h. The colloidal particles are synthesized by the emulsion polymerization method from the monomers of styrene (St), methyl methacrylate (MMA) and acrylic acid (AA). The prepared spheres consist of the hydrophobic PSt core and hydrophilic PMMA-AA shell. The colloidal particles have large amount of negative surface charge due to the COOH groups from the PAA. Furthermore, the PSt core is hard and the PMMA-AA shell is soft due to the PAA swelling in water. The electrostatic repulsion and the adjustable contact surface make the good assembly of colloidal spheres. When the colloidal spheres have assembled to the colloidal photonic crystal (PC), the electrostatic repulsion for separating colloidal spheres disappears, and the soft shells of colloidal spheres cross-link and merge with each other. Thus, inter-particle force are strong enough for resisting washing.

S2. There are different definitions of solvent polarity and several ways to measure it. According to Reichardt,[3, 4] solvent polarity can be defined as the overall solvation capability of solvents, which depends on the action of all possible intermolecular interactions between solutes and solvent, excluding those interactions leading to definite chemical alterations of the solute (such as protonation and oxidation). One of the simplest ways to measure these interactions is by solvatochromic indicators. The most widely used solvatochromic indicator is 2,6-diphenyl-4-(2,4,6-triphenyl-1-pyridinio)-1-phenolate, commonly known as $E_T(30)$ dye or Reichardt's betaine dye since it was proposed by this author.[3, 4] The ground and excited states of the $E_T(30)$ dye present a large difference in dipole moment and therefore the p→p* transition energy of the dye is highly sensitive to solvent polarity. The $E_T(30)$ polarity parameter is defined as the excitation energy (kcal/mol) of the dye in a particular solvent, which can be calculated from the wavenumber (ν_{max} in cm^{-1}) or wavelength (λ_{max} in nm) of the maximum of the absorption spectrum according to the equation:

$$E_T(30)(\text{kcal/mol}) = hc\nu_{max}N_A$$
$$= 2.8591*10^{-3}\,\nu_{max}$$
$$= 2.8591/\lambda_{max}$$

A normalized parameter E_T^N with reference to tetramethylsilane (TMS) ($E_T^N = 0$) and water (H_2O) ($E_T^N = 1$) is recommended instead of $E_T(30)$.[3, 4] E_T^N can be calculated from $E_T(30)$ through

$$E_T^N = \frac{E_T(30) - E_T(30)_{TMS}}{E_T(30)_{H2O} - E_T(30)_{TMS}}$$

Hence, the E_T^N scale ranges from 0.000 for TMS, the least polar solvent, to 1.000 for water, the most polar solvent.[3, 4]. And E_T^N of several common solvents are listed as following:

Solvent	Water	Formanide	Ethanol	2-Propanol	*N*,*N*-Dimethylformamide
E_T^N	1	0.775	0.668	0.546	0.386

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It is seen that the formanide has a relative high polarity in the organic solvents. Therefore, the formanide is chosen for the solvent composition of the PC printing ink.

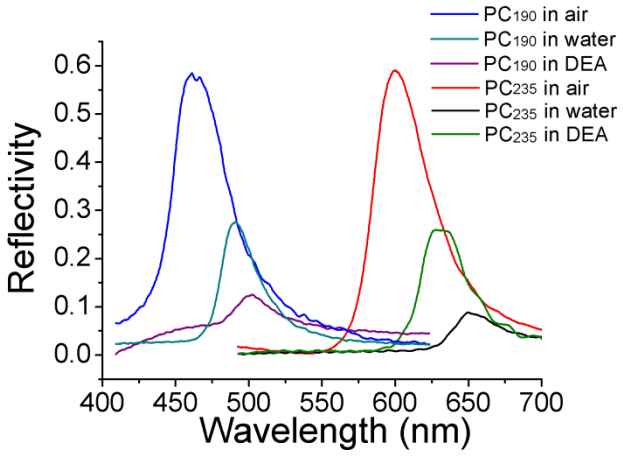

Fig. S3 Reflection spectra of the PC channels (PC_{190} and PC_{235}) in air, water and diethanolamine (DEA). The photonic stop bands of the PCs shown with the wavelength of reflection peaks are responsive to the environment refractive index (n): $n_{air} = 1.0$, $n_{water} = 1.33$ and $n_{DEA} = 1.48$. When the environment refractive index decreased, the wavelength of the photonic stop band blue shifted due to the Bragg's Law ($\lambda = 1.633 \times d \times \sqrt{0.74 \times n_p^2 + 0.26 \times n_{air}^2}$).

The d is the diameter of the colloidal spheres which is 190 nm for PC_{190} and 235 nm for PC_{235}. The n_p is the refractive index of the polymer spheres composed of poly(styrene-methyl methacrylate-acrylic acid), which is *ca.* $n_p = 1.59$. The n_{air} is replaced by n_{water} and n_{DEA} when the PCs are immersed in these solvents. The intensities of reflection peaks increased due to the RI contrasts increasing between the PC and the environment. The sensitivity of the PC microchannel to refractive index change is *ca.* 108 nm/RIU comparable to the reported photonic crystal sensors[1, 2].

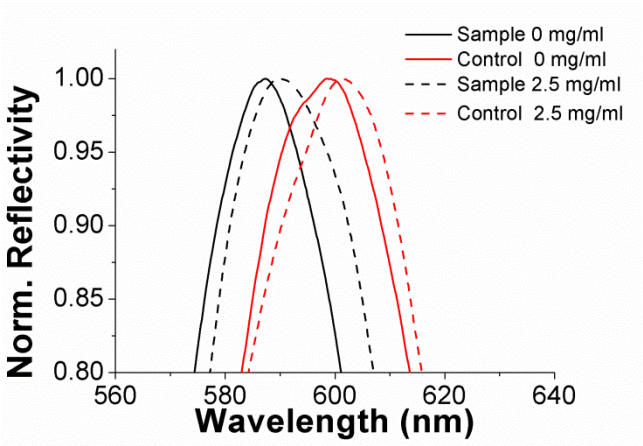

Fig. S4 The normalized reflection spectra of the goat IgG detection. The initial reflection peak wavelengths (λ) of the sample and control spots are 587.34 nm and 598.50 nm after the BSA blocking. When detecting the negative control goat IgG, the λ of sample and control spots red shift to 589.87 nm and 600.98 nm. The Δλ of the sample and control spots are *ca.* 2.53 nm and 2.48 nm. The normalized results excluding the interference of non-specific absorption are *ca.* 0.05 nm which is in the detection error range as <0.09 nm. Thus, the negative control sample as the goat IgG cannot be immune recognized by the surface modified mouse anti human IgG, and the detection are without specific absorption. This result demonstrated that the PC microfluidic assay has the specificity with the specific antibody probe.

References

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4. C. Reichardt, *Chem. Rev.* 1994, **94**, 2319.