Supporting information for

Inkjet Printed Colloidal Photonic Crystal Microdot with Fast Response 5 Induced by Hydrophobic Transition of Poly(N-isopropyl acrylamide)

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Fig. S1 Thermal-responsive UV-Vis transmittance for gel samples with AAm:NIPAm of 10:0, 9:1 and 7:3.

20 The lower critical solution temperature (LCST) of gel samples is determined by UV-Vis spectroscopy at varying temperature. The value was obtained when the abrupt decrease of the transmittance for samples occured. The LCST of the sample with AAm:NIPAm of 9:1 is about 40 °C, and the value is about 38 °C for the sample with AAm:NIPAm of 7:3.

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Fig. S2. The response and recovery time for unit peak shift of PC microdots with different ratios of AAm:NIPAm below or above the LCST.

The amount of hydrophobic groups and phase transition of polymer segments affect the swelling and deswelling process. The increased hydrophobic groups (PNIPAm) reduce the water-adsorption amount, while the hydrophobic transition of PNIPAm above its LCST causes the decrease of adhesion property of water in the polymer interface. Fast swelling and deswelling process is found for the sample (AAm:NIPAm = 9:1) above its LCST due to the decreased water adhesion of polymer segments, while no obvious difference is found for the sample (AAm:NIPAm = 7:3) below and above LCST because of the low swelling degree. The fastest response and recovery rate occurs to the PC microdot with AAm: NIPAm of 9:1.

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Fig. S3 Normalized deswelling ratios for bulk gels of PAAm and PAAm-co-PNIPAm (AAm:NIPAm 9:1) below or above its LCST.

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Deswelling ratios of bulk gels of PAAm and PAAm-co-PNIPAm were obtained by weighing the gel plates at different time after the fully-swollen gels were transferred from water bath to air of the same temperature. The temperature of water bath is 25 °C or 45 °C, respectively.

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Fig. S4 DSC thermograms for bulk gels of (a) PAAm, (b) PAAm-co-PNIPAm (AAm: NIPAm, 9:1)
15 below LCST and (c) PAAm-co-PNIPAm (AAm:NIPAm, 9:1) above LCST at predetermined deswelling periods, respectively. The changing trend of integration of endotherm under different time can explain the distinguished deswelling kinetics of different samples.

AA	AAm:NIPAm	Response (λ _{shift} /time)		Recovery (λ_{shift} /time)	
(n	iolar ratio)	25 °C	45 °C	25 °C	45 °C
	10:0	89 nm/2 s	85 nm/2 s	95 nm/8.5 s	88 nm/8 s
	9:1	76.8 nm/1.2 s	93.8 nm/1.2 s	79 nm/5.2 s	97 nm/1.8 s
	7:3	18.4 nm/0.5 s	9.7 nm/0.25 s	13.1 nm/1.25 s	8 nm/1 s

Table S1 Maximum Bragg diffraction peak shift (λ_{shift}) for colloidal PC microdots during the response/recovery processes under various conditions.

It is found that the colloidal PC microdot with AAm:NIPAm of 9:1 (above LCST) shows the fastest response and recovery process.

Work of adhesion (W_{adh})

Work of adhesion is calculated based on the following equation:¹

 $W_{adh} = \gamma_{LV} (1 + \cos \theta_R)$

Wherein, γ_{LV} is the interfacial tension of liquid and vapor, θ_R is the receding

angle.

In this case, γ_{LV} is 72.75 mN m⁻¹, and θ_R is collected in *Table S2*.

1) L. C. Gao, T. J. McCarthy, Langmuir, 2009, 25, 14105.

Table S2 Wetting parameters of water on the composite responsive colloidal PCs with different monomer ratios.

AAm:NIPAm (mol ratio)/Temperatu	ar Contact re angle	Advancing angle	Receding Angle (θ_R) 24.9°	Hysteresis angle 57.5°
10:0/ <lcst< th=""><th>44.3 ± 1.5°</th><th>82.4°</th></lcst<>	44.3 ± 1.5°	82.4°		
9:1/ <lcst< td=""><td>49.5 ± 1.5°</td><td>62.9°</td><td>40.6°</td><td>22.3°</td></lcst<>	49.5 ± 1.5°	62.9°	40.6°	22.3°
9:1/>LCST	59.6 ± 2.2°	64.1°	51.0°	13.1°

When monomer of AAm/NIPAm in composite colloidal PCs varies from 10:0, 9:1 (below LCST), to 9:1 (above LCST), the adhesion property decreases accompanied with enhanced hydrophobicity.



Fig. S5 In-situ micro-reflectance spectra and optic image (insert) of the colloidal PC microdots upon fluid approaching.

When the fluid is passing through, the colloidal PC microdots change structural color from transparent to bluish green and optic signal red shifts from the weak peak of 450 nm to the strong one of 525 nm.



Fig. S6. Configuration used for real-time monitoring of a microfluidic with PC microdots. (a) microsensing apparatus containing the PC microdots. (b) *In-situ* micro-reflectance spectra of PC microdots recorded as flow amount changes from 0 to 96.0 mm³.

The real-time monitoring of the vapor amount in a microfluidic system is realized by fixing the as-printed PC microdots under the objective lens of a microscope. Micro-reflectance spectra were real-time recorded using an optical fiber spectrometer coupled to the microscope objective lens. In this process, vapor flow with a velocity of 1.6 mm³/s was slowly injected into the microfluidic channel with a volume of *ca*. 78.8 mm³. The PC microdots change color and the optical signal red shifts from a weak peak of 480 nm to a strong one of 545 nm as the vapor flow amount increases from 0 to 96.0 mm³. Accordingly, vapor amount in the microsystem could be real-time determined based on the change of optical signal/structure color and the rapid response of the PC microdots. This sensor provides a facile approach for real-time monitoring of microsystems, and is of significance for the detection of extended reactions in microenvironments.