

## Supporting information

### 1. Glossary

Symbols and the corresponding units in this work:

$C^{av}$	the statistically average concentration of the analyte in mesopore channel, mol/cm <sup>3</sup>
$q$	the statistically average concentration of the analyte in macropore channel, mol/cm <sup>3</sup>
$C_0^b$	the concentration of target species under the saturated vapor pressure, mol/cm <sup>3</sup>
$D_{pore}$	diffusion coefficient inside the pore, cm <sup>2</sup> /s
$L$	the half average length of the tube, cm
$r_{pore}$	the inner radius of mesopore, cm
$R$	the diameter of the used colloidal particle, cm
$H$	the film thickness, cm
$\Gamma_{site}$	the surface concentration of binding sites decorating the mesopore wall, mol/cm <sup>2</sup>
$f(y)$	the distribution function of binding sites inside the pore wall surface
$k_{ads}$	adsorption rate constant, cm <sup>3</sup> /mol/s
$k_{des}$	desorption rate constant, s <sup>-1</sup>
$k_{app-ads}$	the apparent adsorption rate constant, cm <sup>3</sup> /mol/s
$k_{app-des}$	the apparent desorption rate constant, s <sup>-1</sup>
$K_{des}$	desorption equilibrium constant, cm <sup>3</sup> /mol
$\rho, \varphi$	the regulatory factors to describe the molecular imprinting efficiency
$y$	normalized nanopore axial coordinate
$t$	time, s
$\theta$	the local pore wall coverage

$\beta$  the ratio between the molecule and nanopore size

## 2. The average length of nanotube in macro-mesoporous film

When the diameter of mesopore is  $r$ , the diameter of the equivalent sphere is  $R$ , and the thickness of wall is  $d$ , in the cross-section of the equivalent sphere, the number of the tube is:

$$N = \frac{R-d}{r+d}$$

When the number of  $N$  is odd, the length of tube  $l_n$  is:

$$l_n = 2\sqrt{(R/2)^2 - [(n-1)(r+d)]^2}$$

Then the average length of tube is:

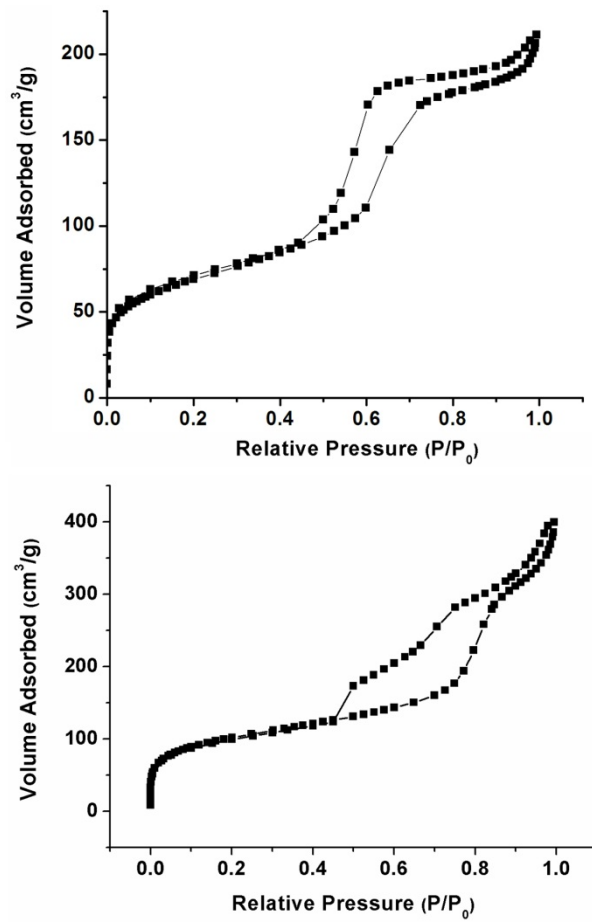
$$L_{av} = \langle l_n \rangle = \frac{R + \sum_{n=2}^{(N-1)/2} 2\sqrt{(R/2)^2 - [(n-1)(r+d)]^2}}{N}$$

When the number of  $N$  is even, the length of tube  $l_n$  is:

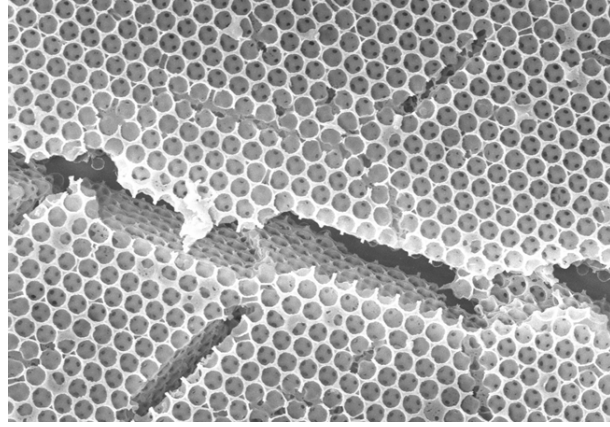
$$l_n = 2\sqrt{(R/2)^2 - [(n-1/2)(r+d)]^2}$$

Then the average length of tube is:

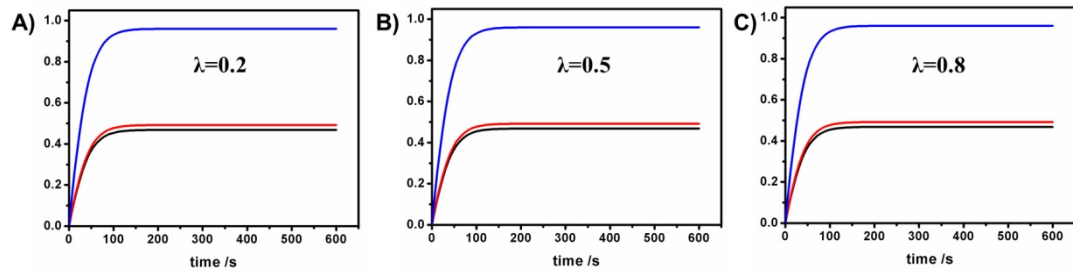
$$L_{av} = \langle l_n \rangle = \frac{2 \sum_{n=1}^{N/2} 2\sqrt{(R/2)^2 - [(n-1/2)(r+d)]^2}}{N}$$



**Figure S1.** N<sub>2</sub> adsorption-desorption isotherms of the synthesized mesoporous (Top) and macro-mesoporous film (Bottom).



**Figure S2.** SEM image of the molecularly imprinted macro-mesoporous film after the extraction of all used templates.



**Figure S3.** Dependence of the sensing behaviors on the variation of  $\lambda$ .  $D_{pore} / L^2 = 13$ ,

$$2\Gamma_{site} / (C_0^b r_{pore}) = 1000, \quad k_{ads} C_0^b = 0.02, \quad K_{des} = 0.085, \quad k'_{ads} = 1.05k_{ads}, \quad K'_{des} = 0.95K_{des},$$

where  $\lambda = 0.2$  for (A),  $\lambda = 0.5$  for (B), and  $\lambda = 0.8$  for (C).