New Journal of Chemistry

Supporting Information

A Polyaniline Inverse Opal/Nanofiber Network Film Fabricated at an Air-water Interface

Likui Wang, Lingyi Jin, Gang Shi, Yun Liu, Bolong Yao, Chengdong Li, Yunxing Li**

The Key Laboratory of Synthetic and Biological Colloids, Ministry of Education, School of Chemical and Materials Engineering, Jiangnan University, Wuxi, 214122, China.

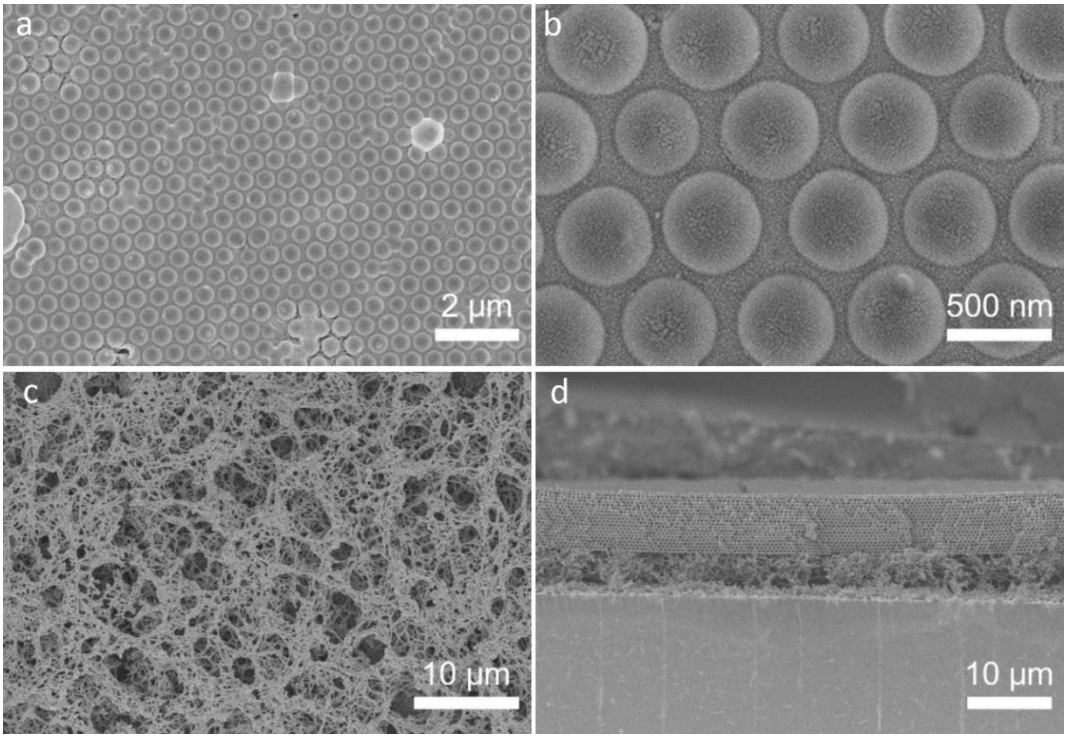

Figure S1. The top view of the PANI coated CC/NFN obtained with m_{APS}/m_{Ani} of 3 (a, b), and the low magnification view of the bottom (c) and cross section (d) of the corresponding IO/NFN.

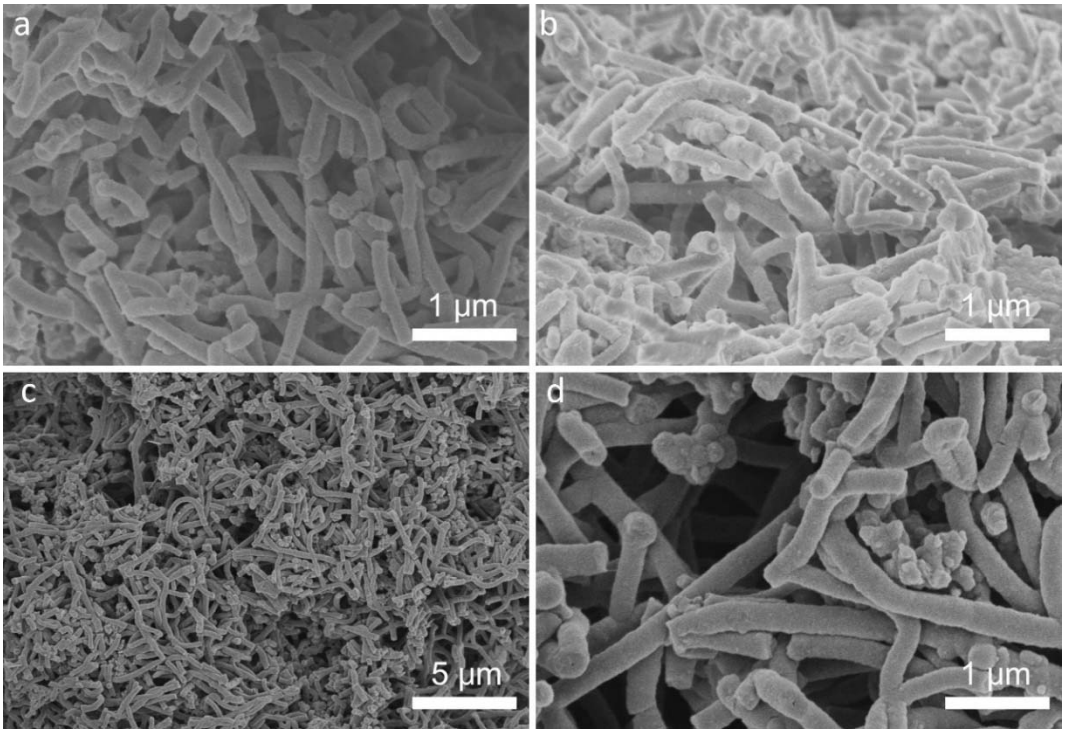

Figure S2. The SEM images of the powders obtained by filtering the solutions after synthesis of the IO/NFNs with m_{APS}/m_{Ani} of 3 (a), 4 (b) and 6 (c and d).

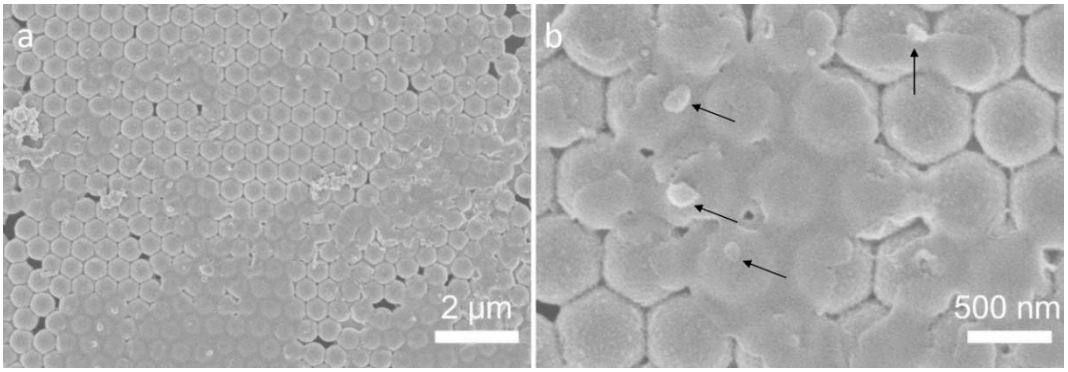

Figure S3. The SEM image of the bottom surface of CC 12 h after addition of APS solution with m_{APS}/m_{Ani} of 3. The nanofiber nuclei are indicated by the arrows.

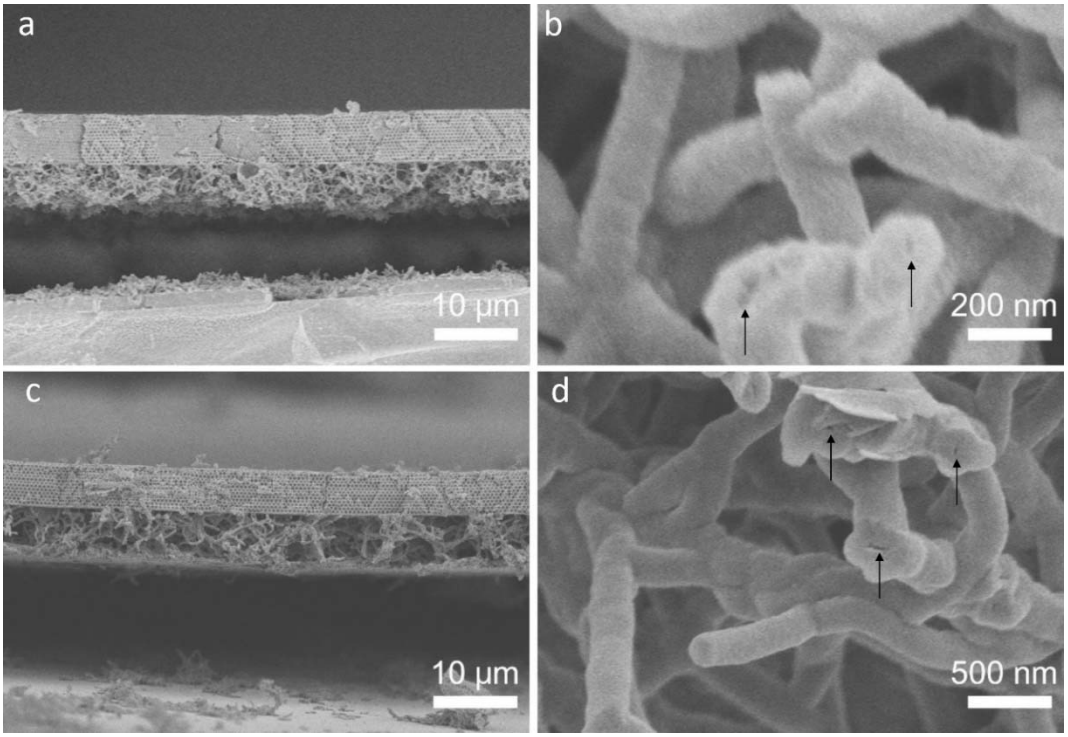

Figure S4. SEM of PANI IO/NFN obtained with *m*APS/*m*Ani of 4 (a, b) and 6 (c, d). The hollow structure of the nanofibers is indicated by the arrows.

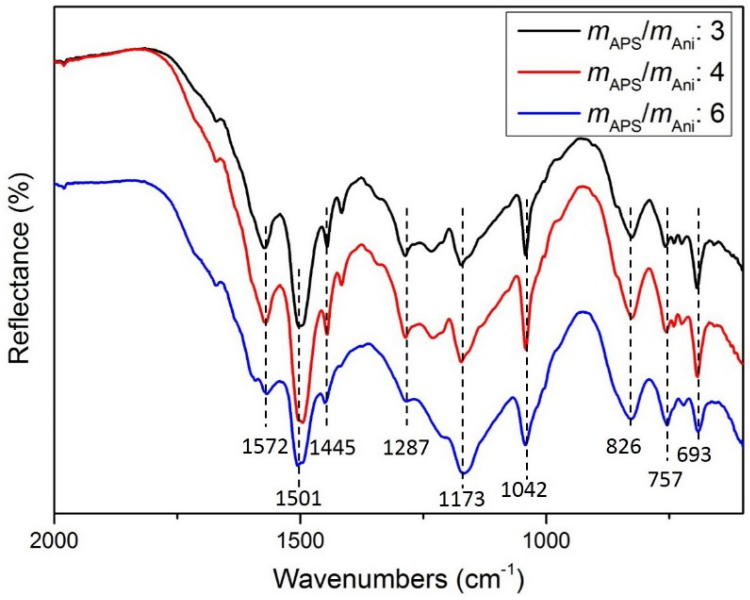

Figure S5. ATR-FTIR spectra of the IO/NFNs obtained from m_{APS}/m_{Ani} of 3, 4 and 6.

The characteristic peaks at 1572 and 1501 cm^{-1} are due to the C=C stretching vibration of benzenoid and quinonoid rings of PANI. The bands at 1445 and 1415cm^{-1} could be assigned to mixed C–C stretching, and C–H and C–N bending vibrations. The peaks at 1287 and 1173cm^{-1} are related to the C–N stretching vibration. The peak at 1042 cm^{-1} is due to aromatic ring deformation. The band at 826 cm^{-1} is out of plane bending of C–H in para-substituted ring. The bands at 757cm^{-1} and 693 cm^{-1} are characteristic of mono-substituted aromatic rings which are located at chain ends.

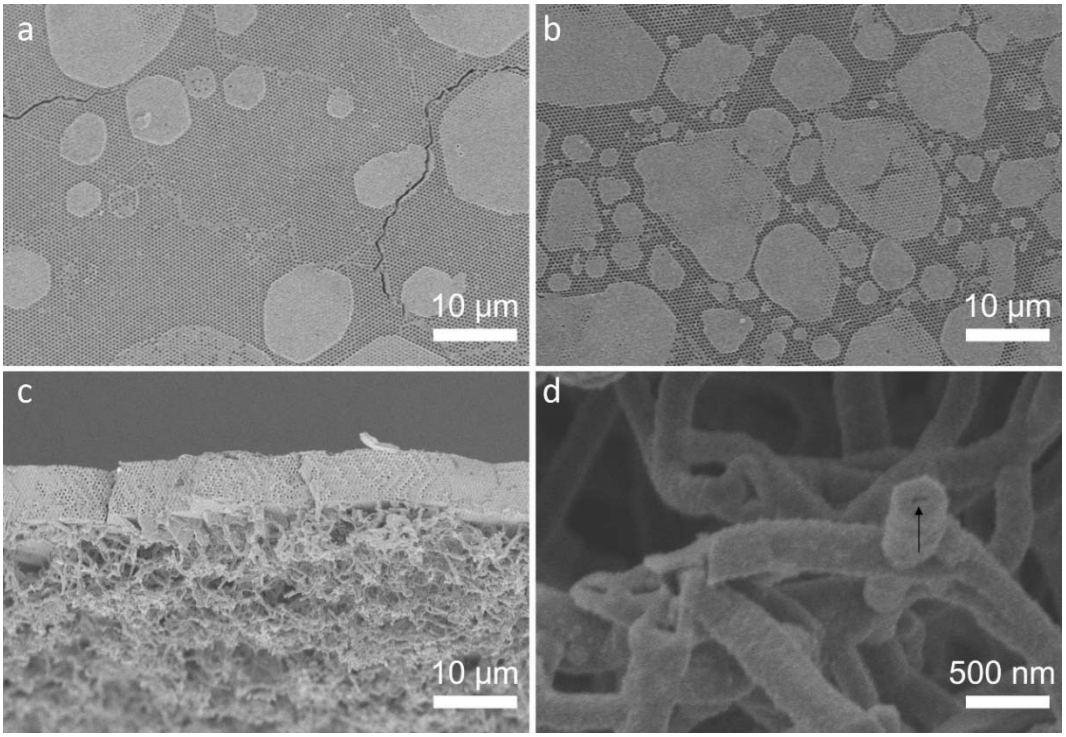

Figure S6. The SEM top view of the IO/NFNs fabricated at aniline concentration of 53.7 mM (a) and 80.5 mM(b). The cross section of IO/NFN obtained from aniline concentration of 80.5 mM (c) and a magnified view of the fibers in the NFN (d).

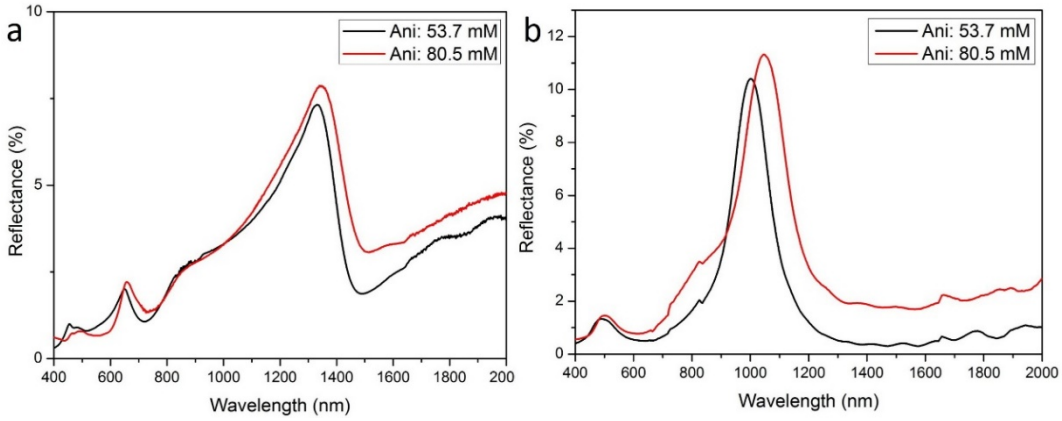

Figure S7. The UV-Vis-NIR spectra of the PANI coated CC/NFNs (a) and the corresponding IO/NFNs (b) prepared with aniline concentration of 53.7 mM and 80.5 mM, respectively.

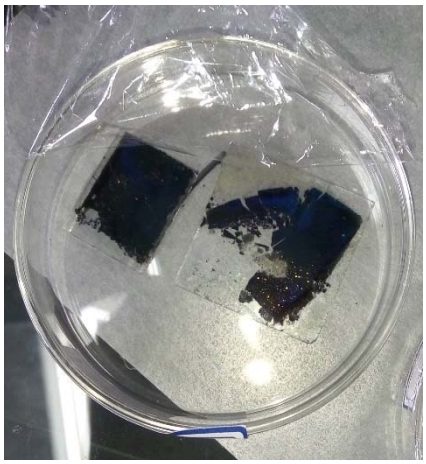

Figure S8. Digital images of the IO/NFN samples obtained with m_{APS}/m_{Ani} of 3(left) and 4(right) from a CC of 536 nm PS spheres contained in a petri dish (60 mm diameter).

The size of the IO/NFN sample obtained with m_{APS}/m_{Ani} of 3 is around 1.35cm × 1.7 cm. During the fabrication process, the colloidal crystals could be broken during the transferring processes and washing process, so did the final sample, as shown in the right image. Normally, a sample of larger than 1 cm × 1cm could be obtained.

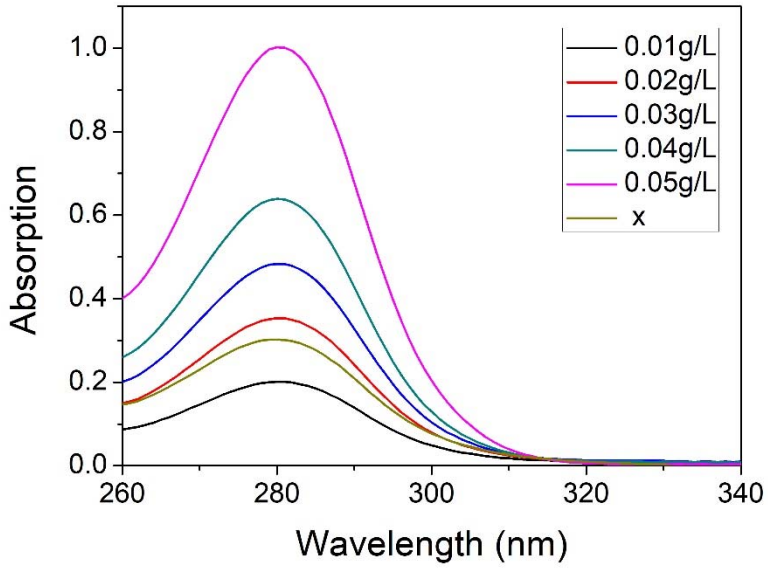

Figure S9. The absorption spectra of aniline solutions with different concentrations and that obtained from a 0.03 g/L aniline solution after swelling the PS spheres.

The measurement of the partition coefficient of aniline for PS/mixture of ethanol and water (4%, v/v): Standard aniline solutions of 0.01 g/L, 0.02 g/L, 0.03 g/L, 0.04 g/L and 0.05 g/L were prepared with mixture of ethanol and water (4%, v/v) and UV-Vis absorption spectra were measured for each samples. PS spheres of 0.15g were added into a 5g 0.03 g/L aniline solution. After sonication, the solution was put in ice water bath for 24h, after which the solution was centrifuged to collect the supernatant clear solution. The UV-Vis absorption spectrum of the obtained solution was also measured, as shown in Figure S9. Through fitting the absorption peak at 280 nm, the aniline concentration of the solution was calculated to be 0.017g/L after addition of PS spheres. Consequently, the partition coefficient of aniline for PS/mixture of ethanol and water (4%, v/v) is 27.5. Which is in good accordance with the solubility parameter analysis.

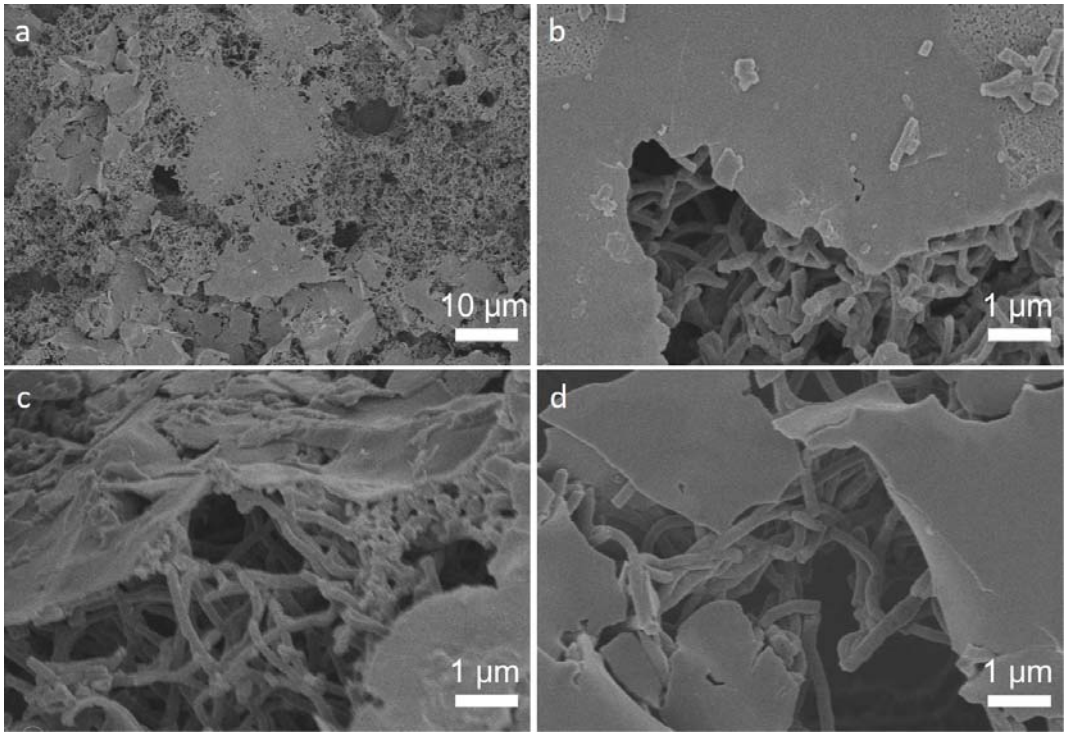

Figure S10. The samples obtained from control experiments without PS CCs floating on the aniline solution surface, with m_{APS}/m_{Ani} of 3 (a, b), 4(c) and 6 (d).

The conductivity of the IO/NFN samples: We have measured the conductivity of the sample obtained with m_{APS}/m_{Ani} of 3, 4 and 6 with a handhold DT830B digital mulitimeter. The electrical resistances between the top and bottom surfaces of all the three IO/NFNs are larger than 2MΩ. This low conductivity should be due to the polymerization without doping agent and with excess oxidant. Without conductivity, the IO/NFNs could still found applications in metal ions adsorption of heavy metal ions, catalyst support, and carbonization for production of N-doped porous carbon materials.

Table S1. Hansen Solubility Parameters of the materials

	δ_D ($MPa^{1/2}$)	δ_P ($MPa^{1/2}$)	δ_H ($MPa^{1/2}$)	δ ($MPa^{1/2}$)
Ethanol	15.8	8.8	19.4	26.5
Water	15.5	16	42.3	47.8
Aniline	19.4	5.1	10.2	22.5
Polystyrene	22.28	5.75	4.3	23.4

* $\delta_D, \delta_P, \delta_H$ are the Hansen Solubility Parameters (HSPs) for the dispersion, polar and hydrogen bonding interactions, respectively. δ is the Hilderbrand Solubility Parameter.

In Table 1, $\delta^2 = \delta_D^2 + \delta_P^2 + \delta_H^2$ and the HSPs of a binary mixture could be calculated by Equation S1:

$$\delta_{blend} = \varphi_{comp1} \times \delta_{comp1} + \times \varphi_{comp2} \times \delta_{comp2} \quad (S1)$$

The δ_D, δ_P, δ_H and δ of the mixture of ethanol and water (4%, v/v) could be calculated to be: 15.5, 15.7, 41.4 and 47.0 respectively.

Table S2. The difference of δ_D, δ_P, δ_H and δ between aniline and different materials

	$\lvert\Delta\delta_D\rvert$ ($MPa^{1/2}$)	$\lvert\Delta\delta_P\rvert$ ($MPa^{1/2}$)	$\lvert\Delta\delta_H\rvert$ ($MPa^{1/2}$)	$\lvert\Delta\delta\rvert$ ($MPa^{1/2}$)
Ani-Water	3.9	10.9	32.1	25.3
Ani-Ethanol	3.6	3.7	9.2	4
Ani-Mixture	3.9	10.6	31.2	24.5
Ani-PS	2.9	0.7	5.9	0.9

* Ani-Mixture means the difference of the solubility parameters between aniline and the mixture of ethanol and water (4%, v/v).

For polypyrrole, it is applicable in fabrication of inverse opals with open pores, without nanofibers attached at their bottom, with this air-water interface polymerization method. Polypyrrole nanofibers normally only forms with the aid of surfactant micelle (Macromolecules, 2005, 38, 7873) or fiber seeds (JACS, 2004, 126, 12714). It's interesting to study whether it is possible to produce polypyrrole IO/NFNs with the aid of surfactant or nanofiber seeds in the future. Currently, the fabrication of IO/NFN is only applicable for polyaniline.