Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Versatile Synthesis of Highly Porous DNA/CNT Hydrogel for the Adsorption of Carcinogen PAH

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Materials and methods

Materials

Salmon sperm DNA (low molecular weight), Benzo[a]pyrene (≥96%, (HPLC)), 1-naphthylamine (≥95%), N,N,N,N-tetramethyl-ethylenediamine (TEMED) and ethylene glycol diglycidyl ether (EGDE) were obtained from Sigma (Shanghai, China). Amino modified multi-walled carbon nanotubes (CNT) were purchase from Jiangsu XFNANO Materials Tech Co., Ltd (Jiangsu, China). N-hexane (anhydrous, 95%) and coronene (95%) were bought from Aladdin Industrial Corporation (Shanghai, China). Sodium hydroxide (NaOH, ≥95%) was purchase from Macklin Biochemical Technology Co., Ltd (Shanghai, China).

Instruments

Scanning electron microscopic (SEM) images were recorded by Phenom Pro X Desktop Scanning Electron Microscope (Phenom, Netherlands). Fourier Transform Infrared spectra (FTIR) were acquired by TENSOR II spectrophotometer (Bruker, Germany). The fluorescence of PAH was identified by F-7100 Fluorescence Spectrophotometer (HITACHI, Japan). Thermogravimetric Analysis (TGA) was acquired by TGA4000 Thermal Gravimetric Analyzer (PerkinElmer, USA). The contact angle was measured using 5 μL droplets on a drop shape analyzer (Data Physics OCA15 Instruments GmbH, Germany). The UV-vis spectra was obtained by U-2910 Ultraviolet-visible Spectrophotometer (HITACHI, Japan). The Zeta potential analysis was recorded by NanoBrook Omni (Brookhaven, USA). The specific surface areas were measured by N_2 adsorption and desorption on Micromeritics ASAP 2460 instrument (Micromeritics, USA).

Synthesis and characterization of porous DNA/CNT hybrid gel

Synthesis of DNA/CNT hybrid gel was carried out based on a previously reported procedure with modifications[1]. DNA (100 mg) was dissolved in Milli-Q water (400 μL) at a room temperature, followed by addition of NaOH solution (0.5 M, 80 μL) and the CNT solution (20 mg/mL, 320 μL). The solution was subsequently mixed with cross-linking agent EGDE (100 μL) and initiator TEMED (10 μL). Oil phase (n-hexane, 1 mL) was added to the mixed aqueous solution, and the resulting two-phase system was shaken vigorously at 50°C for 4 hours. After reaction, the resulting DNA/CNT hybrid gel was freeze-dried under vacuum. For comparison, the non-porous DNA/CNT hybrid gel was synthesized without shaking. To investigate the influence of CNT amount on porosity, the DNA/CNT hybrid gel was prepared with different concentration of CNT (5 mg/mL, 10 mg/mL, 15 mg/mL and 20 mg/mL).

The CNT (20 mg/mL) stabilized emulsions in the reaction solution were imaged by inverted microscopy (NIKON, Ts2) immediately after being prepared by shaking. For SEM observation, a piece of the DNA/CNT hybrid gel was cut from the bulk material, attached to a silicon wafer by conductive tape and treated by spray-gold under vacuum. For FT-IR analysis, the DNA/CNT hybrid gel was grinded before measurement. The thermal stability of DNA/CNT hybrid gel was investigated by thermogravimetric analysis at a heating rate of 10 K/min under a dry nitrogen flow.

Swelling experiment

The swelling characteristic of the DNA/CNT hybrid gel was measured by the following method. The freeze-dried DNA/CNT hybrid gel was immersed in Milli-Q water at room temperature, and the weight was measured at consecutive time intervals. The swelling degree (q_t, g/g) was determined according to the following equation (1).

$$q_t = \frac{W_t - W_d}{W_d} \quad (1)$$

where W_d is the weight of freeze-dried gel (g) and W_t is the weight of swollen gel (g) at a time t.

CNT solubility studies

In order to study the effect of DNA on the dispersity of CNT in water, 64 mg of CNT were immersed in DNA solution (100 mg/mL). Aliquot (200 μL) was taken out from the bulk solution at different time intervals, centrifugated at 10, 000 rpm for 5 min and washed twice with water. The as prepared CNT-DNA was redispersed in water for the UV-vis spectrum measurement and zeta potential characterization. CNT was treated and characterized in the same way as controls.

Adsorption studies

The adsorption of BaP by porous and non-porous DNA/CNT hybrid gel was investigated. Briefly, 2 mg of the gel was put into 100 mL of solution containing BaP (10 ng/mL) under room temperature, and the concentration of BaP was measured at consecutive time intervals by fluorospectrophotometer[2]. The adsorption of coronene by both hybrid gels was determined under the same condition. In order to investigate the effect of initial BaP concentration on their removal efficiency by the porous hybrid gel, BaP solution of different concentrations (1-50 ng/mL) was used for the adsorption experiment.

The removal amounts of BaP (Q_t, μg/g) at t time (h) was calculated according to the following equation (2).

$$Q_t = \frac{(C_0 - C_t)V}{W} \quad (2)$$

where C_0 is the initial concentration of BaP in aqueous solution (ng/mL) and C_t is the concentrations of BaP (ng/mL) at t time (h). V is the volume of the solution (mL) and W is the weight (g) of added hybrid gel.

Furthermore, pseudo-first order and pseudo-second order kinetic models were used to analyze the experimental data. The pseudo-first order kinetic model is represented by the equation (3).

$$\ln(Q_e - Q_t) = \ln Q_e - k_1 t \quad (3)$$

where Q_e (μg/g) is the removed BaP amounts at equilibrium and Q_t (μg/g) is the removed BaP amounts at t time (h); k_1 is the rate constant calculated from the nonlinear curve shown in Fig. 5.

The pseudo-second order kinetic model is represented by the equation (4).

$$\frac{t}{Q_t} = \frac{1}{k_2 Q_e^2} + \frac{1}{Q_e} t \quad (4)$$

where k_2 is the rate constant calculated from the nonlinear curve in Fig. 5.

Adsorption isotherms exploration

The Langmuir and Freundlich adsorption isotherm models were used to describe the equilibrium between the adsorbed BaP on the porous DNA/CNT hybrid gel (Q_e) and the BaP in aqueous solution (C_e)[2]. The linear form of the Langmuir isotherm is represented by the equation (5).

$$\frac{1}{Q_e} = \frac{1}{K_L Q_m} \cdot \frac{1}{C_e} + \frac{1}{Q_m} \quad (5)$$

Where Q_m is the maximum adsorption capacity and K_L is the equilibrium constant of Langmuir adsorption.
The Freundlich model is nonlinear and it can be expressed by the equation (6).

$$\ln Q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (6)$$

where K_F is the Freundlich constant representing the adsorption capacity and n is a parameter regarding the intensity of adsorption.

CNT adsorption capacity investigation

To explore the adsorption capacity of CNT in the hybrid material, the percentage of CNT surface coverage was investigated using 1-naphtylamine, an organic molecule that can only be absorbed by CNT[3]. CNT, CNT-DNA, DNA/CNT hybrid gel and pure DNA gel were put into 10 mL of solution containing 1-naphthylamine (20 µM), respectively. The concentration of 1-naphthylamine was measured at different time intervals by Ultraviolet-visible Spectrophotometer. In the experiment, the amount of CNT in all samples was kept the same (50 µg).

Supplementary Figures

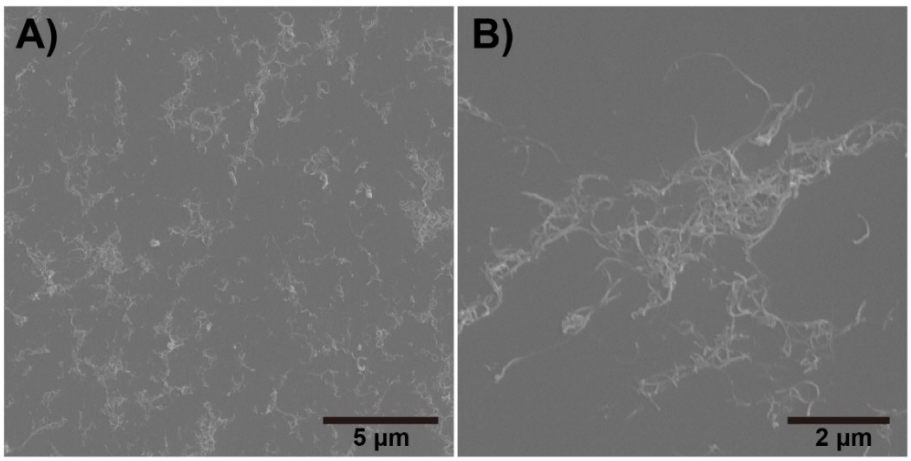

Fig. S1 SEM images of CNT under low (A) and higher magnification (B).

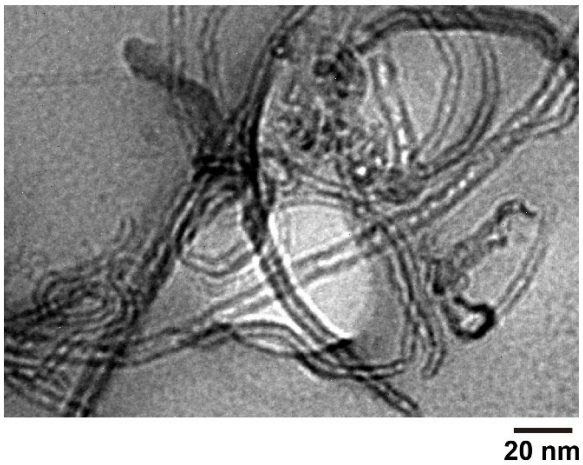

Fig S2 TEM image of CNT dispersed in deionized water.

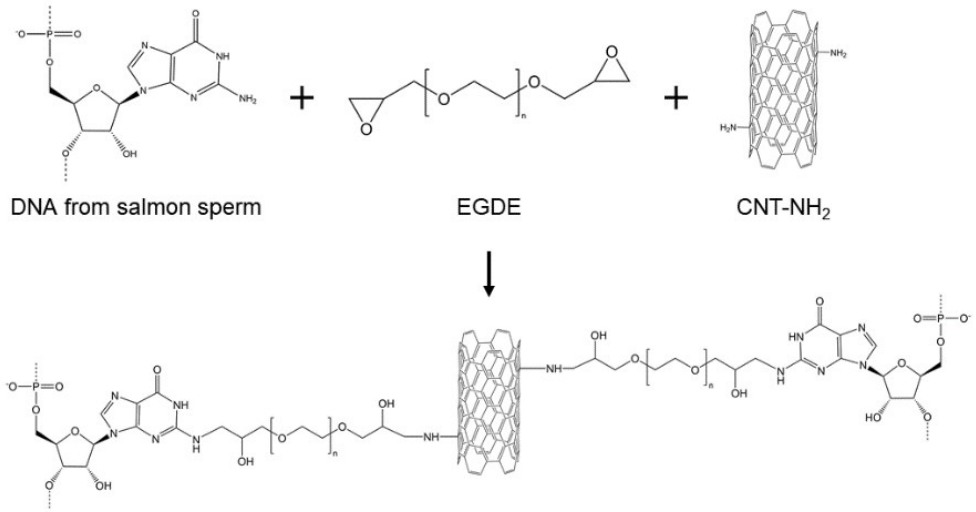

Fig. S3 Chemical cross-link reactions between DNA and CNT.

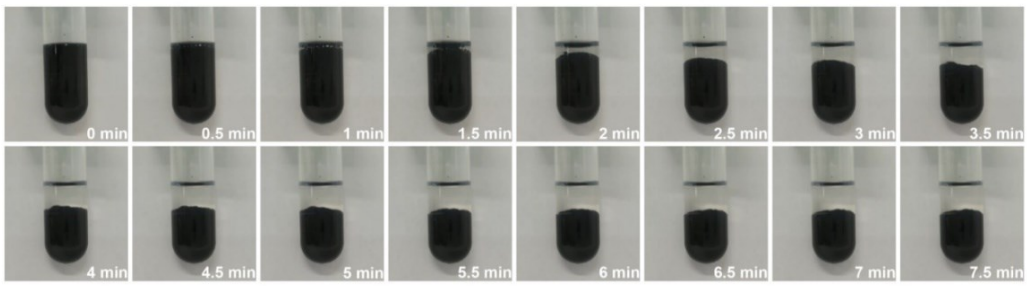

Fig. S4 Photographs of the standing Pickering emulsion taken at different time interval.

Fig. S5 Photographs of CNT (left) and CNT-DNA (right) dispersed in aqueous solution.

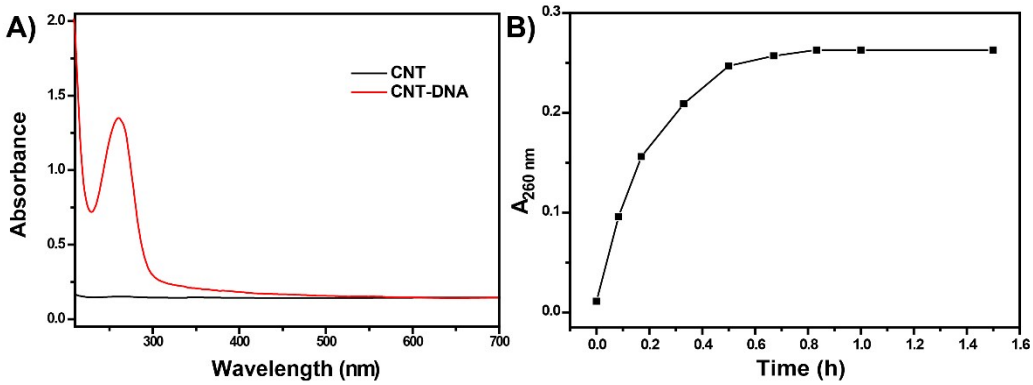

Fig. S6 (A) UV–vis absorption spectra of CNT and CNT-DNA solution. (B) Variation of CNT-DNA absorption at 260 nm with different interaction time.

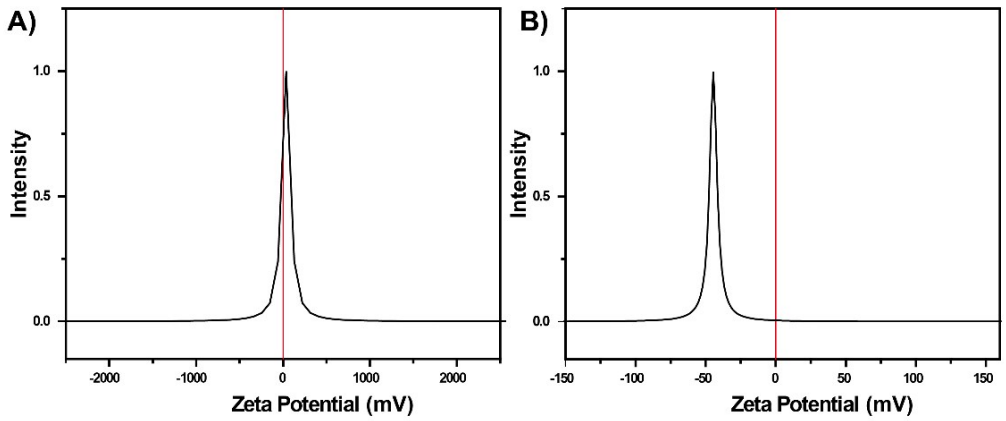

Fig. S7 Zeta potential of CNT (A) and CNT-DNA (B) solution.

Fig. S8 Water contact angle measurement of CNT-DNA.

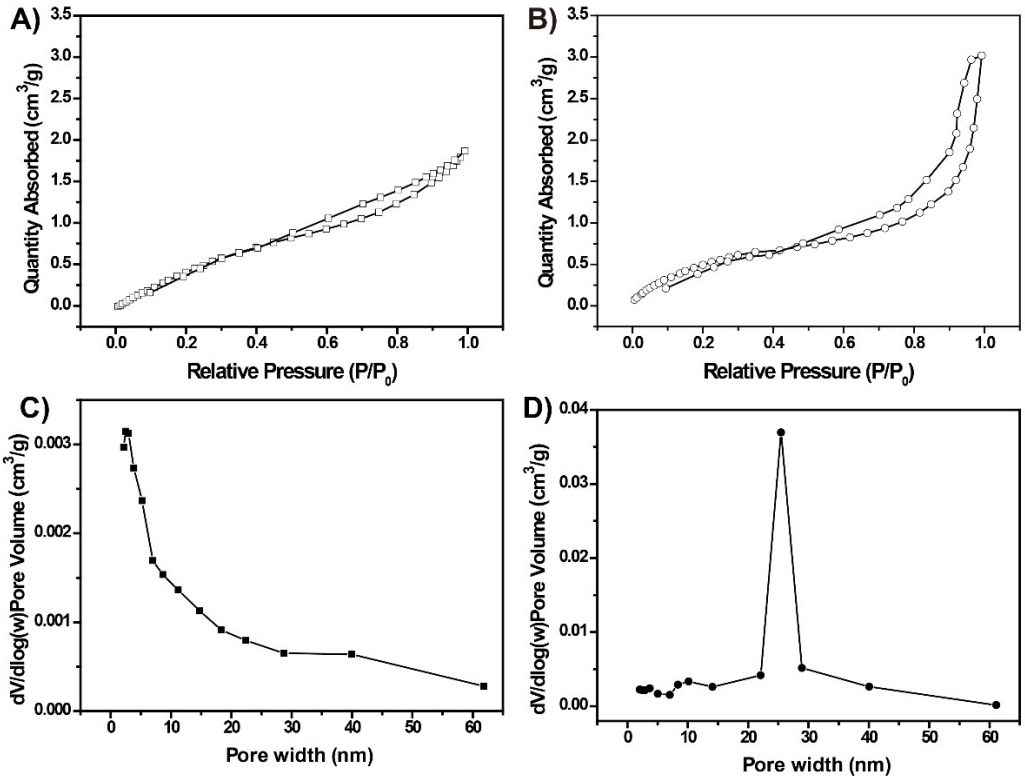

Fig. S9 Nitrogen adsorption-desorption isotherms (A, B) and pore size distributions (C, D) for non-porous (left) and porous (right) DNA/CNT hybrid gel.

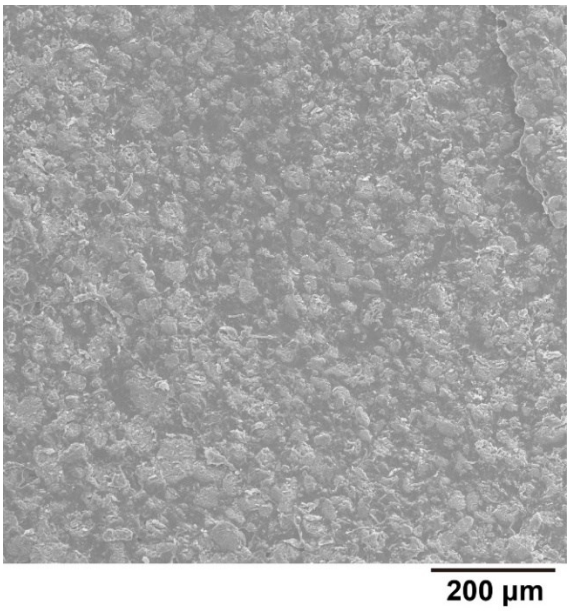

Fig. S10 SEM image of non-porous DNA/CNT hybrid gel prepared with 20 mg/mL CNT.

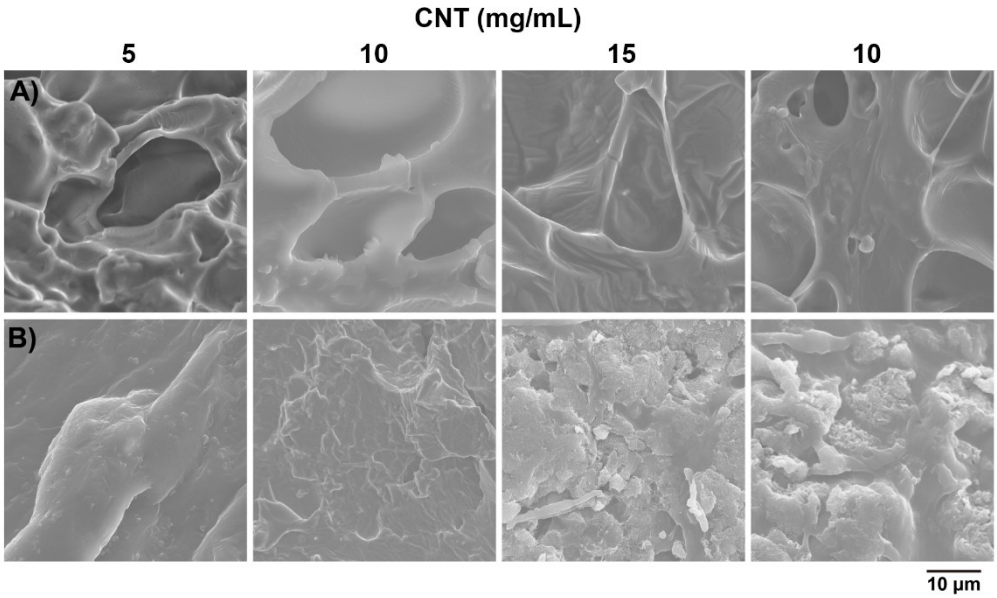

Fig. S11 SEM images of (A) porous and (B) non-porous DNA/CNT hybrid gel containing 5 mg/mL, 10 mg/mL, 15 mg/mL and 20 mg/mL CNT.

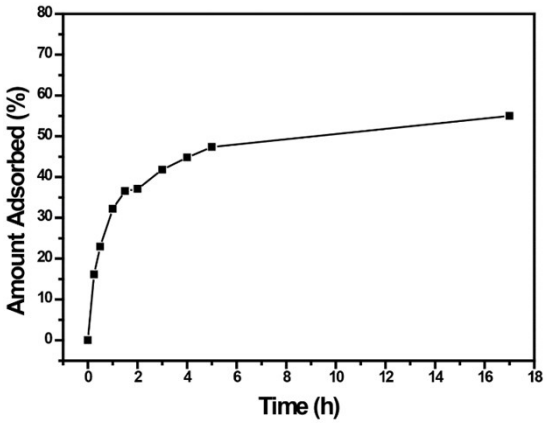

Fig. S12 Time-dependent adsorption curve of BaP (10 ng/mL, 100 mL) by pure DNA gel (2 mg). For comparison, the experiment was carried out under the same conditions as the adsorption assays of porous and non-porous DNA/CNT gel.

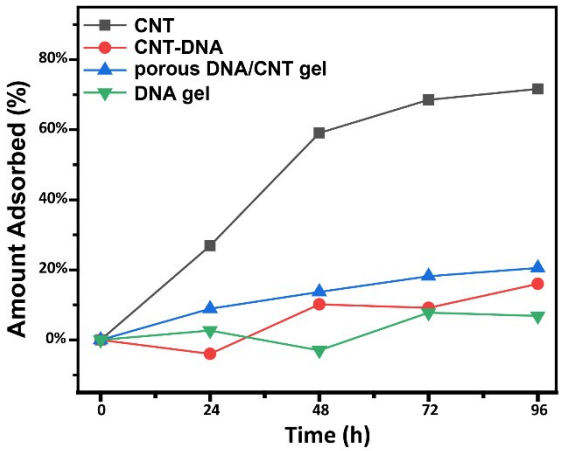

Fig. S13 Change in the adsorption efficiency of CNT (black line), CNT-DNA (red line), porous DNA/CNT (blue line) and pure DNA gel (green line) for 1-naphtylamine (20 μM, 10 mL) over the time. Compared with CNT (71.6%), CNT-DNA displayed significantly reduced adsorption efficiency (16%) due to the passivation of DNA on its surface. Interestingly, the porous DNA/CNT hybrid gel showed slightly higher adsorption of 1-naphtylamine (20.5%) in comparison with CNT-DNA. This phenomenon can be probably ascribed to the physical trapping of 1-naphtylamine by the porous structure of the gel.

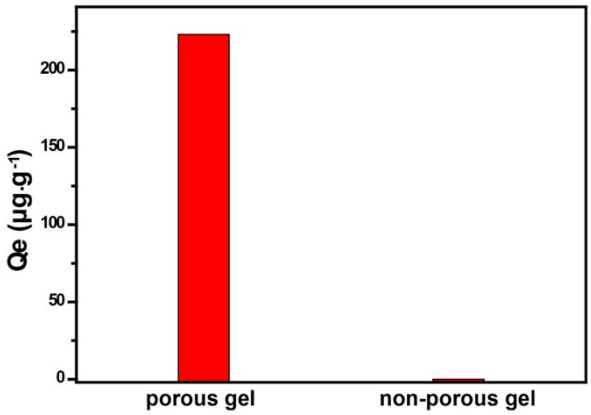

Fig. S14 Adsorption capacity of porous and non-porous DNA/CNT hybrid gel (2 mg) for coronene (10 ng/mL, 100 mL).

Table S1. Parameters of Sorption kinetics of BaP on porous and non-porous DNA/CNT hybrid gel fitted by the pseudo-first order model and pseudo-second order model.

Gel type	Kinetic model	q_e (μg/g)	k	R^2
porous	pseudo first-order kinetic model	306.98	0.67	0.995
	pseudo second-order kinetic model	389.99	0.00164	0.998
non-porous	pseudo first-order kinetic model	252.6	0.493	0.999
	pseudo second-order kinetic model	341.8	0.00123	0.999

REFERENCES

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2 X. Deng, K. Lin, X. Chen, Q. Guo and P. Yao, *Chemical Engineering Journal*, 2013, **225**, 656–663.
3 A. Zinchenko, Y. Taki, V. Sergeyev and S. Murata, *Nanomaterials*, 2015, **5**, 270–283.