

Supporting Information

Interaction of Tannic Acid with Carbon Nanotubes: Enhancement of Dispersibility and Biocompatibility

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1. Materials and methods

1.1 chemical structure of tannic acid

TA was purchased from Sinopharm Group Chemical Reagent Co.Ltd (Shanghai, China) with a structure characterized as five digallic acid units ester-linked to a glucose core (contained in red curve, Fig. S1). It has a large number of phenolic hydroxyl groups with a molecular weight of 1701 ($C_{76}H_{52}O_{46}$) and a solubility of 300 g L^{-1} in water. Due to its unique structure, TA could strongly interact with CNTs via π - π interactions (between bulk π systems on CNT surfaces and tannic acid with benzene rings) and hydrogen bonds (because of the functional groups on CNT surfaces).

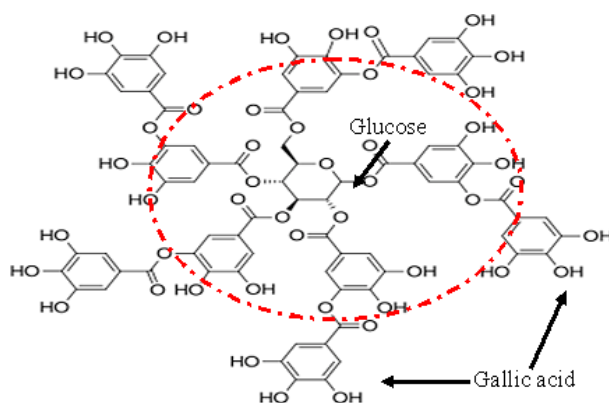


Fig. S1 Chemical structure of tannic acid, a deca-galloyl glucose consisting of a center glucose molecule esterified at all five hydroxyl moieties with two gallic acid molecules.

1.2 Characterization of CNTs

SWNT and MWNT40 were characterized by SEM and TEM, the detail characterization procedure were displayed below. The microstructure of SWNT and MWNT40 was characterized by scanning electron microscopy (SEM, LEO 1530 vp) and transmission electron microscopy (TEM; JEOL, JEM-2010). CNT samples were prepared by placing a droplet of MWCNT aqueous suspension on silicon substrate and 300 mesh copper carbon grid for SEM and TEM examination. All of these MWCNT samples were dried overnight at $60 \text{ }^\circ\text{C}$ under vacuum before observation.

1.3 Determination the concentration of TA

The filtrate was immediately determined by a Uv-Vis spectrophotometer at 274 nm and the concentrations of TA were calculated with the following equation ($y=0.07732+0.0364x$, $r^2=0.997$). Moreover, the adsorption capacity q (mg/g CNTs) were obtained as follows: $q = [(Co - Cf)V/m]$; where Co and Cf are the initial and final concentrations (mg/L) of TA in the aqueous solution, respectively, V is the volume of TA solution and m is the weight of CNTs.

1.4 Equilibrium time of sorption

The equilibrium time of adsorption between CNTs and TA were investigated by using MWCNT40. Briefly, 11.8 mg MWCNT40 was mixed with 59 mL of TA solution, which concentration is 40 $\mu\text{g/mL}$. After shaking with different time, the TA adsorbed by CNT was determined by Uv-vis spectrometer (Hitachi, U-3010, Tokyo, Japan) at the wavelength of 274 nm.

1.5 Cytotoxicity of TA

The cytotoxicity of TA to A549 cells were conducted according to the procedure as described in the manuscript. The cytotoxicity of different concentrations of TA (5-100 $\mu\text{g mL}^{-1}$) were determined.

2. Results

2.1 SEM images of SWNT and MWNT40

The SEM Images of SWNT and MWNT 40 were displayed in Fig. S2a and Fig. S2b, respectively.

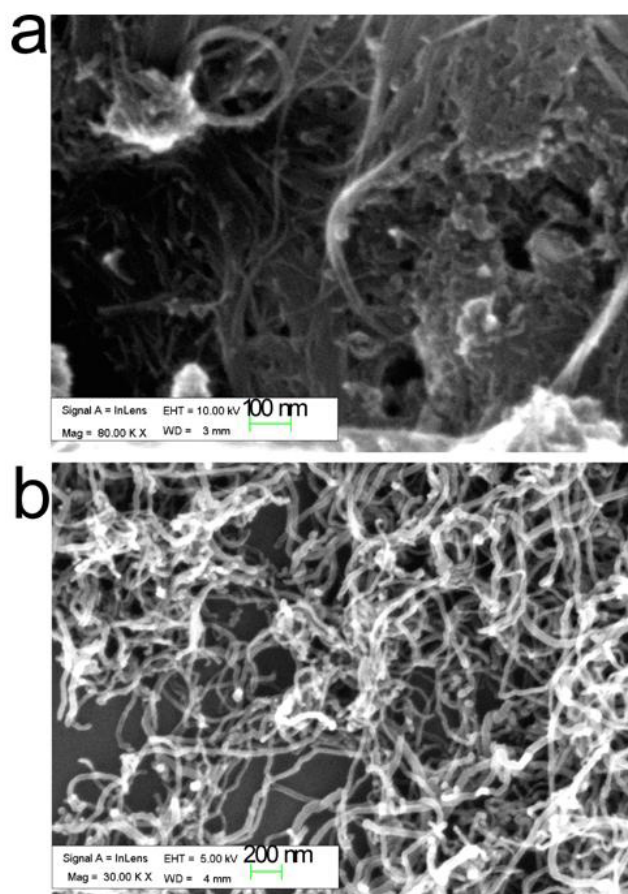


Fig. S2 SEM images of CNTs a) SWNT, scale bar = 100 nm; and b) MWNT40, scale bar = 200 nm

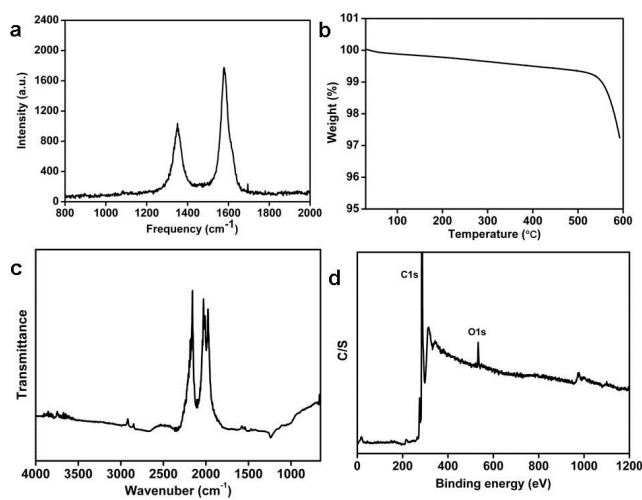


Fig. S3 Characterization of MWNT40. a) Raman spectrum, b) TGA, C) FT-IR, d)XPS.

2.2 Determination the concentration of TA

UV-Vis spectrometer was used to determination the concentration of TA, as shown in Fig. S4a, TA has a obvious absorbance peak at the wavelength of 274 nm, the concentrations of TA showed good

linear relationship with the absorbance at 274 nm, (standard equation is $y=0.07732+0.03642x$, $r^2=0.997$).

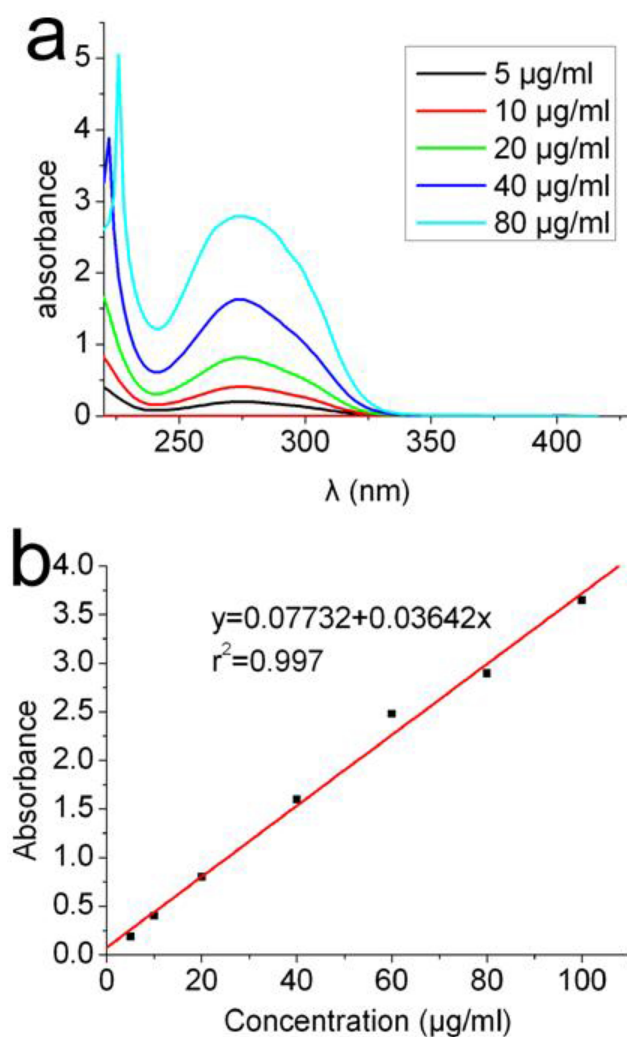


Fig. S4 a) UV-Vis spectrum of TA with different concentration (5-80 $\mu\text{g mL}^{-1}$), the wavelength range was 190-460 nm, b) linear standard curve between the concentrations of TA and the absorbance at 274 nm.

2.3 Equilibrium time of sorption

Before, the sorption experiments, the equilibrium time was first determined by using MWNT40 as model materials. It can be seen that, the adsorption of TA on MWNT40 is very fast, only first 4 h, the concentration of TA on the CNT was reached to about 65 mg/g. after 48 h, the sorption was achieved to

equilibrium, the adsorption capability is 92 mg/g . This result is important because we could use it to design further sorption experiments.

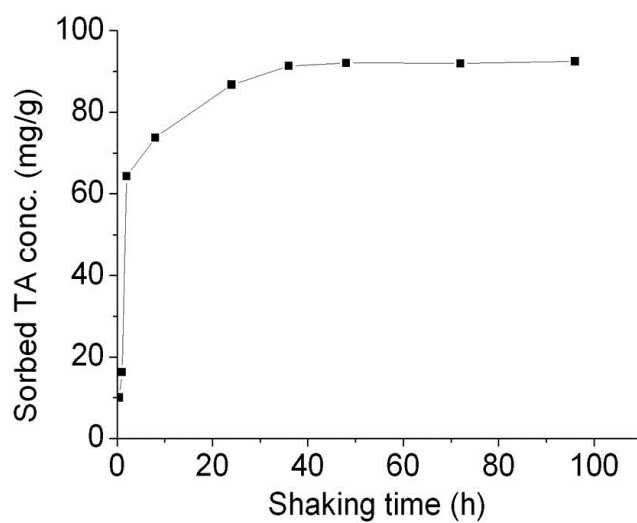


Fig. S5 Equilibrium time of TA adsorption by MWNT40, the concentration of MWNT40 is 200 $\mu\text{g mL}^{-1}$, and the concentration of TA is 40 $\mu\text{g mL}^{-1}$.

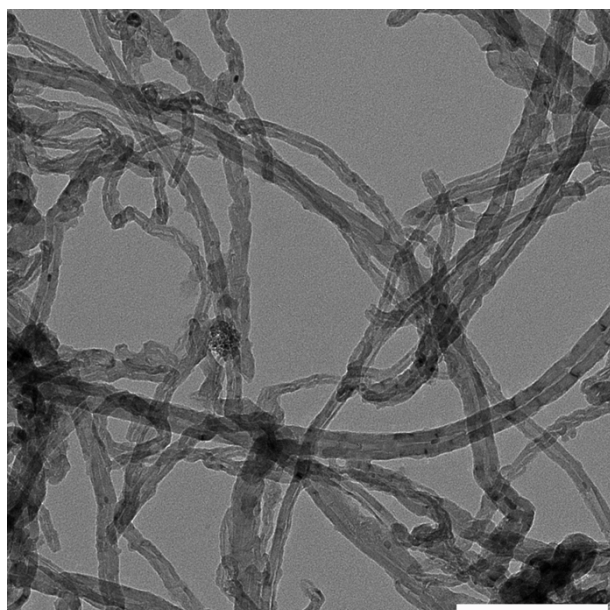


Fig. S6 TEM image of MWNT40-TA, the mass ratio of MWNT40 to TA is 5:1, scale bar =200 nm.

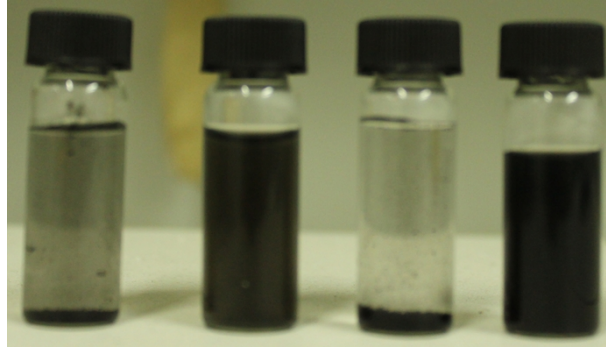
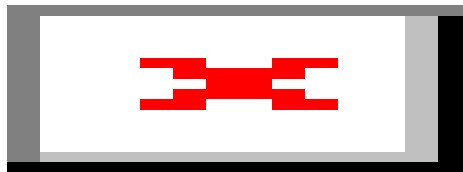


Fig. S7 Optical images of CNT dispersion in water after they were deposited for 5 h, concentrations of CNTs and TA are 200 and 40 $\mu\text{g mL}^{-1}$, respectively. From left to right are the samples of SWNT, SWNT-TA, MWNT40 and MWNT40-TA, respectively.

Table S1. Nonlinear isotherm models

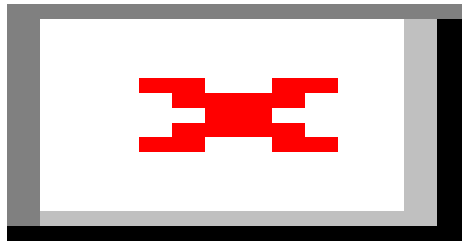


* q_e (mg/g) is equilibrium sorbed concentration; C_e (mg/L) is equilibrium solution phase concentration.

2.4 effects of pH values on sorption

To investigate the pH values on the adsorption capability of TA by CNTs, seven pH values were obtained by adding NaOH/HCl, the detail pH values were displayed in Table S2.

Table S2 pH values after adjustment



2.5 Cytotoxicity of TA

Fig. S8 displays the cytotoxicity of TA to A549 cells after exposure cells to different concentrations of TA to cells for 24 h, obvious dose-dependent cytotoxicity was obtained. However, we could also see that, the cell viability is remained above 90% when the concentrations of TA are below 20 $\mu\text{g mL}^{-1}$. It is therefore when we investigated the effects of TA on the cytotoxicity of SWNT and MWNT40, 20 $\mu\text{g mL}^{-1}$ of TA was used.

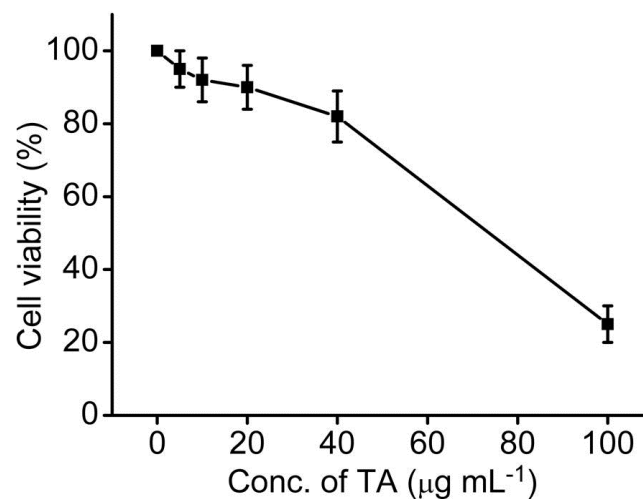


Fig. S8 Cytotoxicity of TA to A549 cells, cells were exposed o 5-100 $\mu\text{g mL}^{-1}$ of TA for 24 h.