Supplementary Information

Materials and chemicals

Copper (II) acetate (CuAc₂) was purchased from Alfa Aesar (Ward Hill, MA). Multi-wall carbon nanotubes with an average diameter of 20-40 nm and an average length of 1 μ m were purchased from Shenzhen Nanotech Port Co., Ltd (Shenzhen, China). Deionized water was purified by a Milli-Q system (Milford, MA, USA). Histidine, tryptophan, sucrose and glucose were purchased from Shanghai Chemical Reagent (Shanghai, China). All other chemicals and reagents were the highest grade and commercially available.

The small metabolites analyzed by MALDI-MS were prepared as followings. Histidine, tryptophan, sucrose and glucose were dissolved in deionized water at a concentration of 1.0 mg/mL. lauric acid and myristic acid were dissolved in a mixture of water and ethanol (1:1, v:v) at a concentration of 0.5 mg/mL.

Synthesis of the MWCNTs@PANI composites

Before combination to polyaniline, multi-wall carbon nanotubes need to be treated with nitric acid to be activated. First, a total of 50 mg multi-wall carbon nanotubes were introduced into 10 mL aqueous solution of nitric acid (3 moL/L). Then the suspension of MWCNTs was ultrasonated for 10 min, followed by the collection of MWCNTs by centrifugation at 8500 rpm for 3 min. The treated MWCNTs were washed by deionized water until the supernate was neutral. Finally the materials were dried in the vacuum drying oven at 50 °C overnight.

In order to eliminate the interference of O_2 in the polymerization process, the deionized water was initially degassed by bubbling with dry N_2 for 30 min. A total of 16 mL aqueous solution of $Cu(Ac)_2$ (0.075 mM) was added into a 200 mL reaction vessel. Afterwards, 64 mL aqueous solution of aniline (0.015 mM) was transferred to the vessel, and almost immediately, the reaction mixture turned into dark green due to the coordination of Cu^{2+} and aniline. Finally, 5 mg multi-wall carbon nanotubes were introduced in the vessel. The polymerization of aniline took place at 180 °C for 4 h under hydrothermal conditions, and the vessel subsequently cooled to ambient temperature naturally. The resulting MWCNTs@PANI suspension was centrifuged at 8500 rpm for 3 min to isolate MWCNTs@PANI composites. The materials were collected and washed with deionized water and ethanol, and then dried in the vacuum drying oven at 50 °C.

Characterizations

Transmission electron microscopy (TEM) images were taken on a JEOL 2011 microscope (Japan) operated at 200kV. Scanning electronic microscope (SEM) images were recorded on a Philips XL 30 electron microscope (Netherlands) operating at 20 kV. Powder X-ray diffraction (XRD) patterns were recorded on a Bruker D4 X-ray diffractometer with Ni-filtered Cu K α_{\Box} radiation (40 kV, 40 mA). Fourier transform infrared spectra (FT-IR) were collected on Nicolet Fourier spectrophotometer using KBr pellets (USA). The Raman spectra were recorded at a room temperature on a LabRam-1B Raman spectrometer with a laser at an excitation wavelength of 632.8 nm.

Applications in the analysis of metabolites by MALDI-TOF-MS

The mass spectrometry measurements were performed by 5800 MALDI-TOF/TOF Mass spectrometer (Applied Biosystems) with nitrogen lasers. The matrix solution of MWCNTs@PANI composites was prepared at a concentration of 1 mg/mL in ethanol/water solution (1:1). 1 μ L water solution material was deposited on the MALDI target plate, which would dry in the air and form a thin layer in few minutes. Afterwards, 1 μ L analyte solution was subsequently dispensed on the plate and dried naturally, and then analyzed by MALDI-TOF-MS.



Fig. S1 TEM image of MWCNTs@PANI composites with a high resolution.



Fig. S2 The FT-IR spectra of pristine MWCNTs (curve a) and MWCNT@PANI composites (curve b).



Fig. S3 Raman spectra of MWCNTs (a) and MWCNTs@PANI composites (b).



Fig. S4 the UV spectra of MWCNTs and MWCNTs@PANI composites.



Fig. S5 The mass spectra of histidine $(m/z=193.9 [M+K]^+)$ glucose $(m/z=218.80 [M+K]^+)$ and lauric acid $(m/z=199.08 [M-H]^-)$.