Electronic Supplementary Material (ESI) for Chemical Communications

Supporting Information

Au-Impregnated Polyacrylonitrile (PAN)/Polythiophene (PTH) Core-Shell Nanofibers with High-Performance Semiconducting Properties

Lijie Wang, Jiahuan Hu, Hongyu Zhang, and Tong Zhang*

Experimental

The highly doped SiO_2 wafers with a 300 nm thermal oxide wafer followed was cut into pieces (2 cm × 1.8 cm), n-octadecyltrichlorosilane (OTS) was used as the second insulator. In a typical procedure, 8 wt% of polyacrylonitrile and certain amount of $HAuCl_4$ were dissolved in DMF, under vigorous stirring at 50 °C for 2 h. After cooled to room temperature, the mixture was loaded into a glass syringe and connected to high-voltage power supply. 12 kV was provided between the cathode and anode at a distance of 15 cm. Two parallel aluminum plates were used for collecting aligned nanofibers during the electrospinning process. Gas-phase polymerization of polythiophene was carried out at 100 ^oC in saturated thiophene (C_4H_4S) vapor to obtain Au-doped PAN/PTH core-shell nanofibers, using $HAuCl_4$ in the as-spun nanofibers as oxidant. Top-contact electrodes were fabricated by thermal evaporation of Au (thick of 50 nm) onto nanofibers.

The images of Au-doped PAN/PTH core-shell nanofibers were obtained by scanning electron microscopy (SEM) measurements which were performed on a JEOL JSM-7500F microscope. Transmission electron microscope (TEM) images were obtained on a HITACHIS-570 microscope with an accelerating voltage of 200 kV. XRD patterns were obtained with a Siemens D5005 diffractometer using Cu KR radiation. Fourier transform infrared spectroscopy (FT-IR) spectra of the film were recorded on a BRUKER VECTOR22 Spectrometer. UV-vis spectroscopy was performed on a Shimadzu UV-2101 PC Spectrometer.

The current–voltage (*I–V*) characteristics of the polymer nanofiber FETs were measured with a Keithley 4200SCS semiconductor parameter analyzer in a clean and metallically shielded box at room temperature in air.

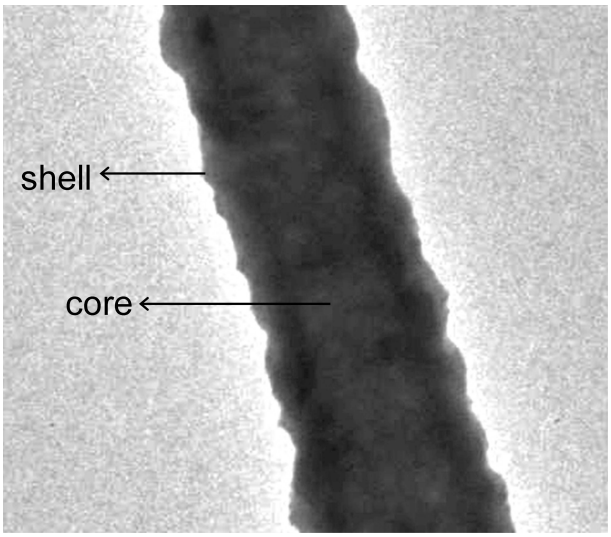

Fig. S1 Enlarged TEM images of the Au-doped PAN/PTH core-shell nanofibers **C**.

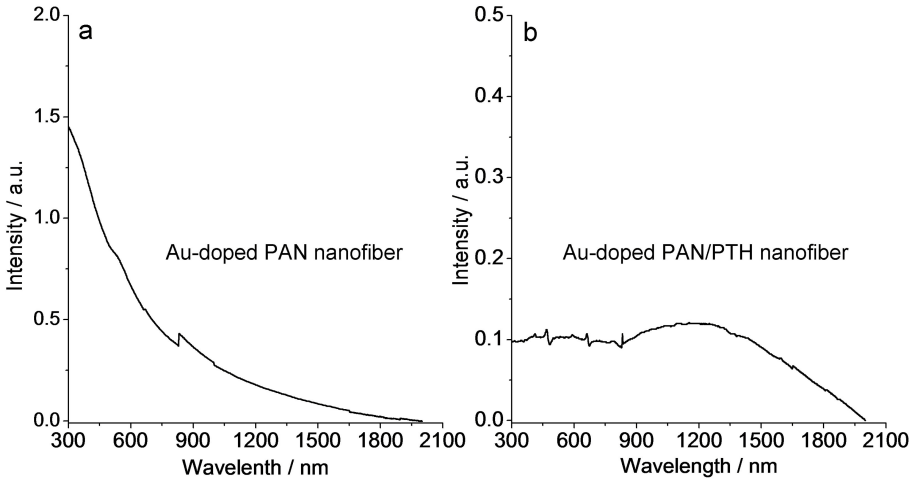

Fig. S2 UV-vis-NIR absorption spectra of the Au/PAN (a) and Au-doped PAN/PTH core-shell nanofibers (b).

In order to test the possibility of the metallic charge transport, we carried out electrical conductivity characterization of the Au nanoparticle-doped PAN fibers (the contents of the $HAuCl_4$ precursor and device configurations are the same as those of Au-doped PAN/PTH core-shell nanofibers) based on direct current-voltage (*I–V*) measurement. Firstly, we prepared PAN/$HAuCl_4$ composite nanofibers by electrospinning, and then reduced the $HAuCl_4$ by hydrazine. The TEM image of the Au-impregnated PAN fibers is shown in Fig. S3. The *I–V* curves of the Au nanoparticals doped PAN nanofibers are shown in Fig. S4. The measured currents are at very low level ($< 10^{-12}$ A) when the applied voltage reach 10 V, which indicated that the Au nanopartical-doped PAN nanofibers are not metallic charge transport. Upon increasing the content of the $HAuCl_4$ precursor, there in no obvious enhancement of the current, further demonstrating the impossibility of the metallic charge transport of these nanofibers. In this sense, the present Au-doped nanofibers are suitable candidates for application in field-effect transistors. We also tested the transporting properties of these nanofibers by fabricating the FET devices, as shown in Fig. S5. It is obvious that the Au doped PAN nanofiber based FET did not display typical transistor behavior.

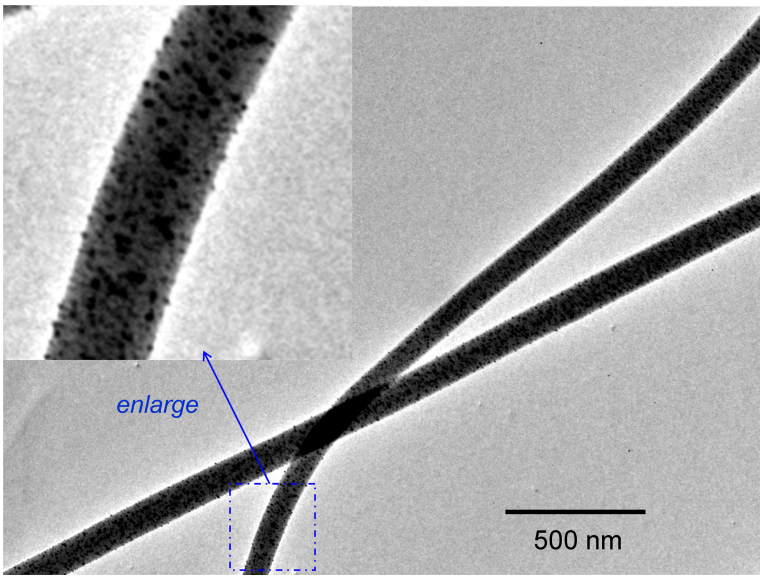

Fig. S3 The TEM image of Au-impregnated PAN nanofibers **C** (the content of $HAuCl_4$ precursor (wt%): 33.3%).

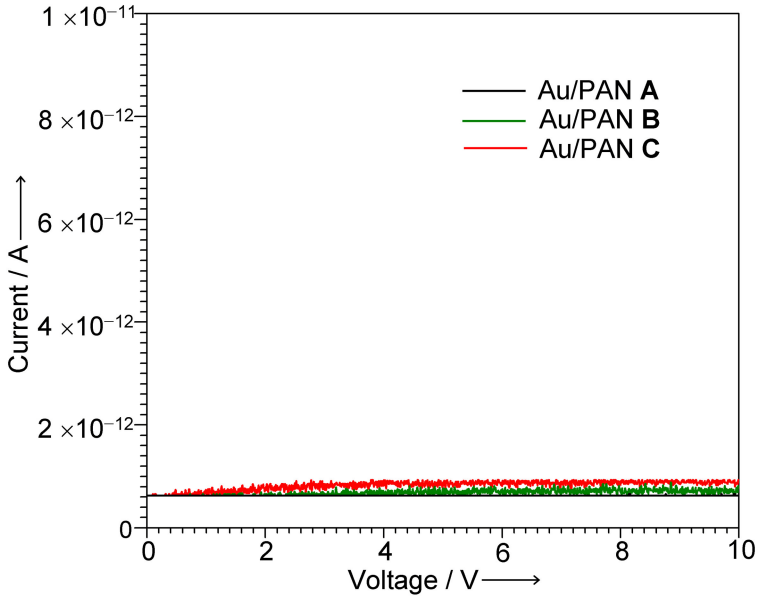

Fig. S4 The *I–V* curves of the Au nanoparticals-doped PAN nanofibers (the content of $HAuCl_4$ precursor (wt%): 16.7% for **A**, 25% for **B**, and 33.3% for **C**).

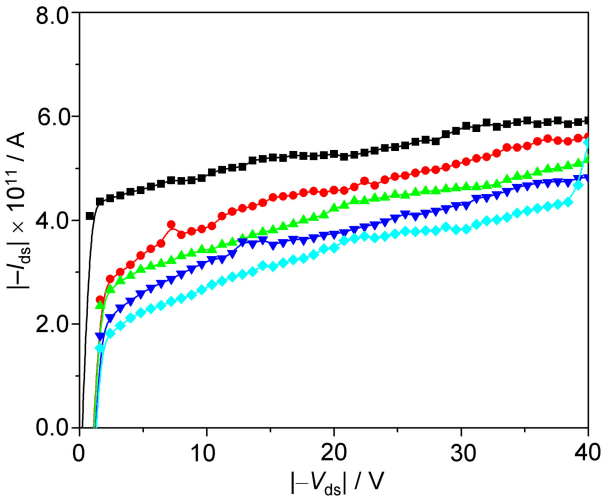

Fig. S5 Plots of drain-to-source current (I_{ds}) vs drain-to-source voltage (V_{ds}) for the FET fabricated by Au nanoparticals-doped PAN nanofibers.

In order to confirm the participation of Au in charge transport, we prepared polyacrylonitrile (PAN)/polythiophene (PTH) nanofibers without Au nanoinclusions by replacing $HAuCl_4$ for $FeCl_3$ which also created doped PTH but does not form Au conducting nanoparticles. In the case of the Au-impregnated PAN/PTH nanofibers **C**, the mass ratio of $HAuCl_4$ to PAN is 1/2 in the electrospinning step. It is to say that the molar ratio is about 0.064/1. During the process of PTH polymerization, the Au^{3+} is reduced to Au^0, while Fe^{3+} is reduced to Fe^{2+}. So we fabricated $FeCl_3$/PAN composite nanofibers, in which the molar ratio was 0.192/1 (3 times of that of $HAuCl_4$/PAN), by electrospinning. Fig. S6 shows the field-effect properties of the as-prepared PAN/PTH nanofibers (using $FeCl_3$ in the as-spun PAN nanofibers as oxidant). The mobility ($\sim 2\times10^{-3}$ cm^2/Vs) is much smaller than that of Au-impregnated PAN/PTH nanofibers **C** ($\sim$2.0 cm^2/Vs). We also turned the content of $FeCl_3$ concentration in the initial step and studied the effect, but the field-effect properties of all the samples are poor. This control experiment indicates that Au in the PTH does play a crucial role in improving the field-effect properties.

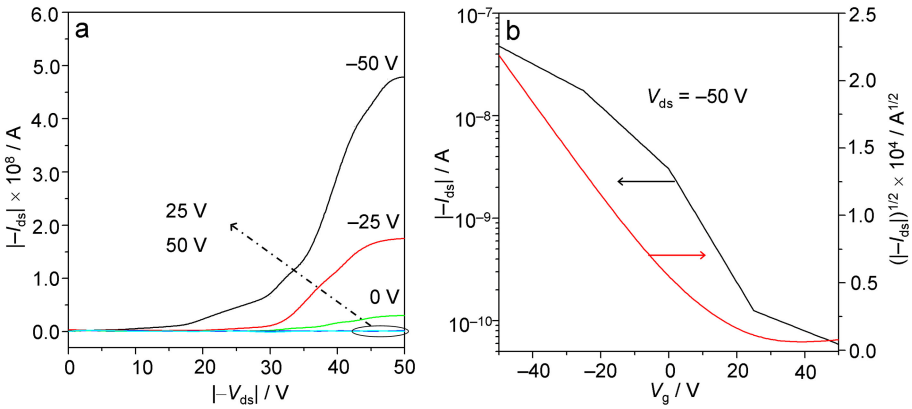

Fig. S6 (a) Plots of drain-to-source current (I_{ds}) vs drain-to-source voltage (V_{ds}) for the FET fabricated by as-prepared PAN/PTH nanofibers (using $FeCl_3$ in the as-spun PAN nanofibers as oxidant). (b) I_{ds} vs V_{gs} plots for the same device at V_{ds} of –50 V.