

Supplementary Information for:

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Shape-Controlled Polyaniline Chemiresistors for High-Performance DMMP Sensor: Effect of Morphologies and Charge-Transport Properties

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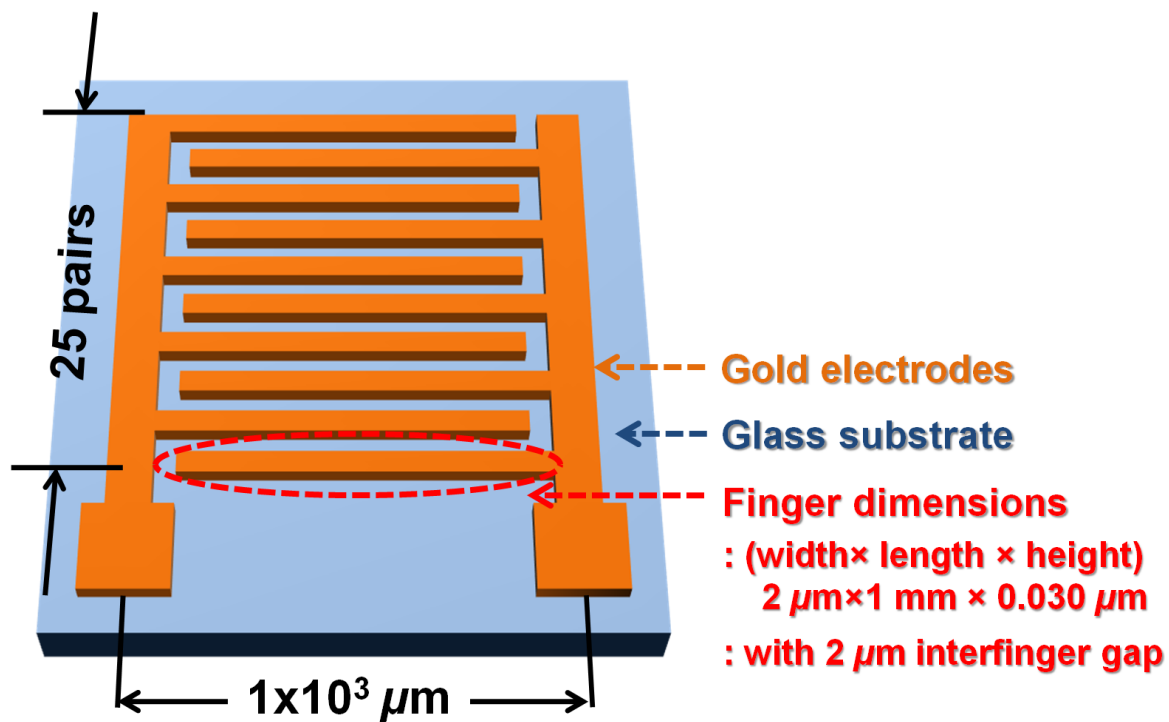
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Table S1. BET Surface areas of PANI nanomaterials obtained by N₂ adsorption/desorption characteristics

sensing materials	aspect ratio	surface area (m ² g ⁻¹)	total pore volume (cm ³ g ⁻¹)
nanofibers	≈25	35.3	0.15
nanorods	≈7.5	40.2	0.17
nanoparticles	≈1.5	46.4	0.19

Gold-interdigitated microelectrode used for DMMP sensor



Scheme S1. Schematic illustration of the interdigitated microelectrode used

Ultraviolet/visible/near-infrared (UV/VIS/NIR) and Fourier-transform infrared (FTIR)
spectra of PANI nanomaterials

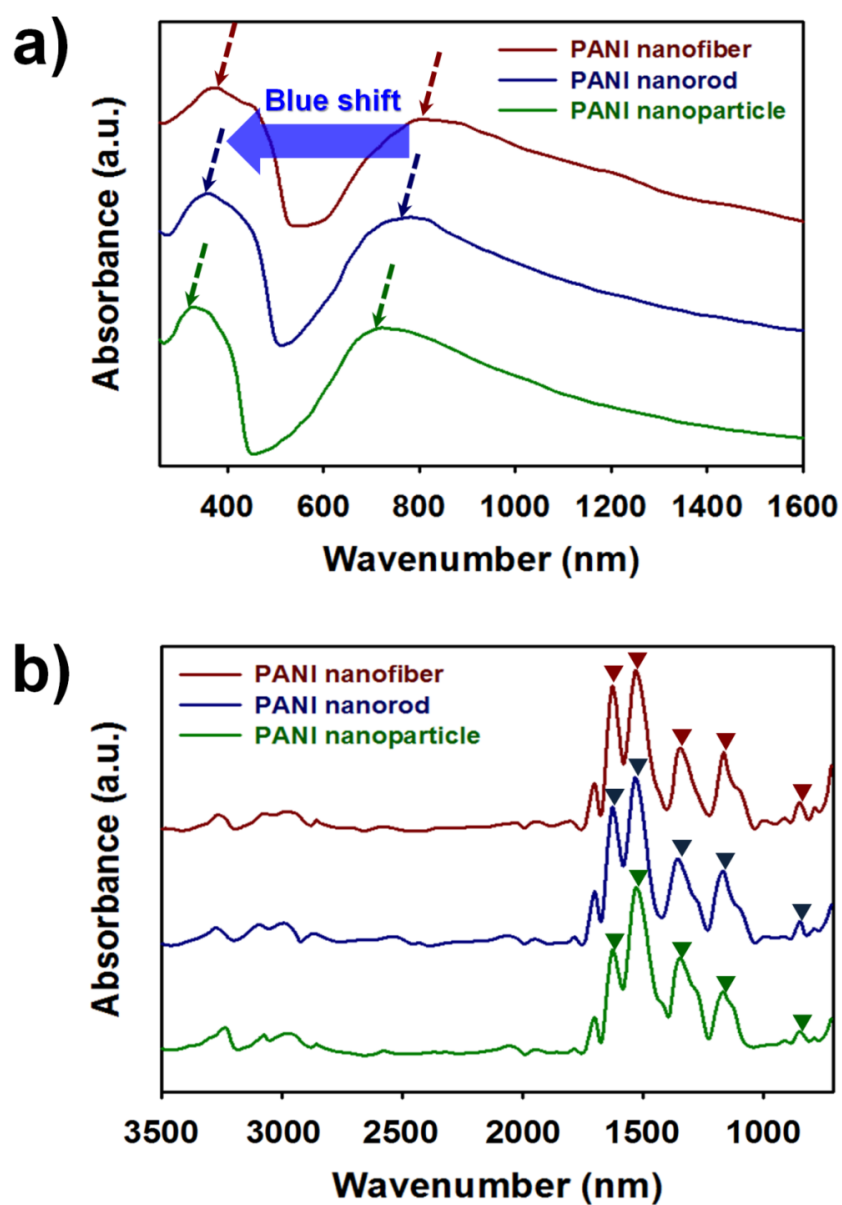


Figure S1. Distinctive bands in (a) UV/VIS/NIR and (b) FT-IR spectra of PANI nanomaterials with different morphologies

Two characteristic bands for emeraldine salts were found in every PANI UV/VIS/NIR spectrum (Figure S1a).^{S1,S2-S4} The absorption bands at 371 and 798 nm for the nanofiber were assigned to π - π^* excitation of the *para*-substituted benzenoid segment ($-\text{B}-\text{NH}-\text{B}-$) and the quinone diamine structure ($-\text{N}=\text{Q}=\text{N}-$), respectively.^{S3} These two bands appeared at 365 and 790 nm, respectively, for the nanorods. Therefore, the doping levels in the nanofibers and nanorods are likely similar. These two bands appeared at shorter wavelengths for the PANI nanoparticles. The bands for the benzenoid segment ($-\text{B}-\text{NH}-\text{B}-$) and the quinone diamine unit ($-\text{N}=\text{Q}=\text{N}-$) of the nanoparticles were slightly blueshifted to 340 and 720 nm. The decrease in the maximum absorption wavelength of the PANI nanoparticles is attributable to a reduced extent of π conjugation within the PANI structure.^{S5} FTIR spectra provide information on the influence of chemical bonding on the charge-transport properties of the PANI nanomaterials (Figure S1b). The band at 825 cm^{-1} originates from the C-H out-of-plane bending of 1,4-disubstituted ring structures (*para*-coupling); these structures result from the favored head-to-tail (HT) coupling during aniline polymerization. The bands at 1145 and 1581 cm^{-1} are attributable to the stretching vibration of the quinone-diamine segment ($-\text{N}=\text{Q}=\text{N}-$). These two bands appeared more prominently in the oxidized form of the nanofibers and nanorods than in the overoxidized PANI nanoparticles. This implies that the PANI nanomaterials become conductive through protonation of the imine nitrogens ($-\text{N}=\text{}$). Additionally, the peaks at 1145 and 1581 cm^{-1} are indicative of the ability to delocalize electrons within the PANI structure.^{S5,S6} The peak at the 1299 cm^{-1} originates from the stretching vibration of C-N in the secondary aromatic amine. This band was more intense for the nanofibers and nanorods than for the nanoparticles, indicating the presence of higher amounts of amine nitrogen that could participate in hydrogen bonding with DMMP. The band at about 1498 cm^{-1} was assigned to C=C stretching in the benzenoid rings ($-\text{B}-\text{NH}-\text{B}-$).

I-V characteristics of PANI nanomaterials

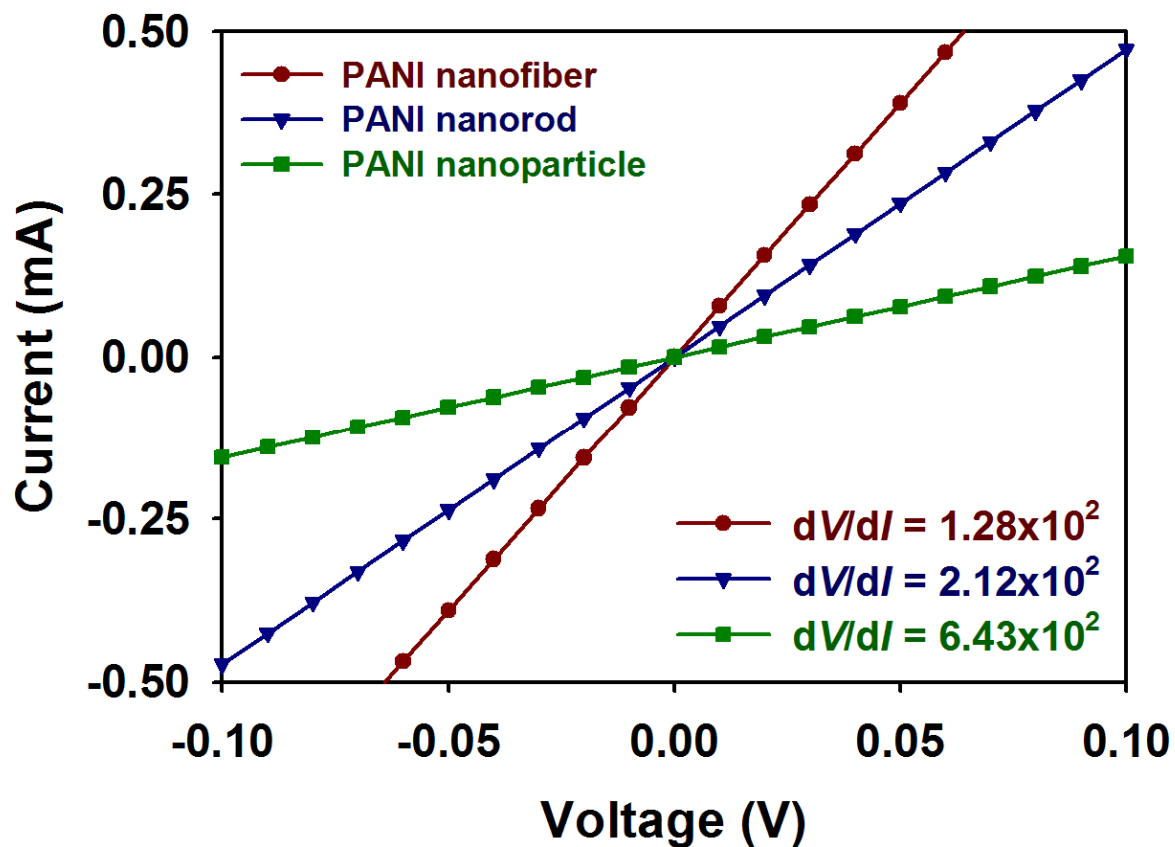


Figure S2. *I-V* characteristics of PANI nanomaterials (0.1 wt% in ethanol) integrated in the sensor substrate at a scan rate of 10 mV s^{-1}

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