Supplementary Information: Giant negative terahertz photoconductivity in controllably doped carbon nanotube networks

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Transmission Electron Microscopy of chemically doped samples

The TEM image of a pristine SWCNT film shows the morphology of randomly oriented individual CNTs and bundles with a small number of CNTs per bundle (Fig. S1a)). The $HAuCl_4$-doped SWCNTs show the presence of dopant nanoparticles on the surface of the tubes (Fig. S1 b,c).

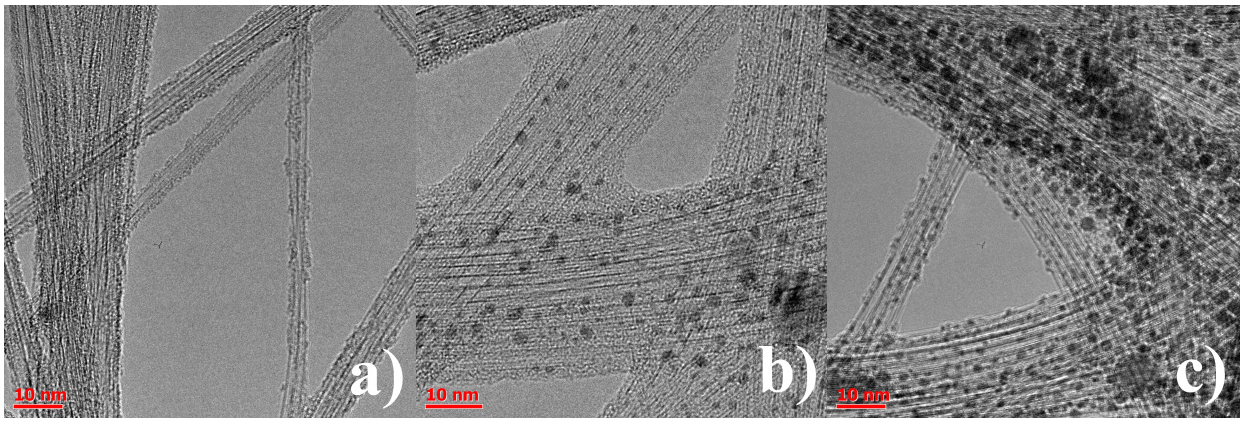

Figure S1: Transmission electron microscopy image of a) pristine and b),c) doped samples with different concentrations of the dopant.

Positive and negative photoconductivity

The sign of the photoconductivity was checked using a semi-insulating GaAs wafer, which shows a reduction in transmission after photoexcitation (negative $\Delta E/E$) as a result of the enhanced free carrier density. The THz pulse for free space, for the pristine SWCNT and GaAs samples before and after excitation are presented in Fig. S2.

Thin film transmission expression

Here we provide a derivation of the expression used to determine the conductivity of the CNT films, valid for doped materials and at large $\Delta E/E$. For a film of thickness d and complex refractive index n_j the transmission from medium 1, with refractive index n_i, into

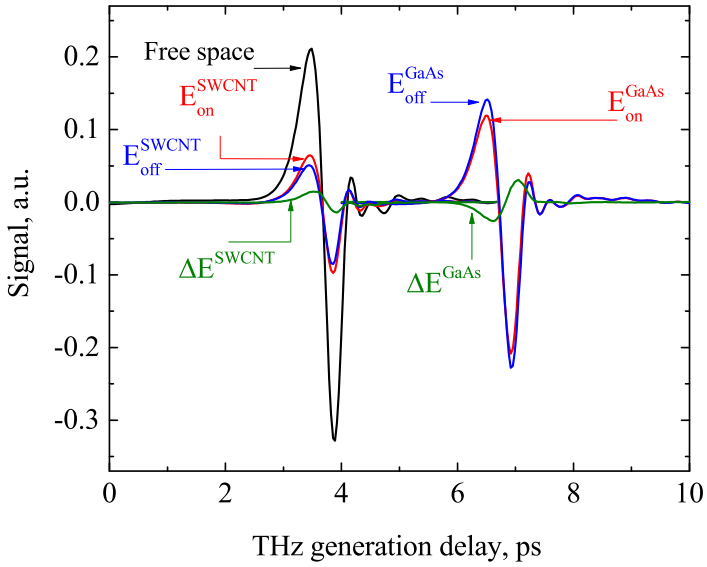

Figure S2: The THz signal without the sample (free space), and for the pristine SWCNT sample and a GaAs wafer. The change of the signal at the THz peak position is positive for the SWCNT and negative for GaAs.

medium 2, with n_j, and then medium 3, n_k, is (at normal incidence):

$$T_{ijk}(\omega) = \frac{2n_i n_j}{n_j \cos\phi_j [n_i + n_k] - i \sin\phi_j [n_j^2 + n_i n_k]}, \tag{1}$$

where $\phi_j = n_j \omega d/c$. This can be simplified in the *thin-film limit*, such that $n_j \omega d/c \ll 1$ and $\kappa_j \omega d/c \ll 1$, to

$$T_{ijk}(\omega) = \frac{n_i + n_k}{n_i + n_k - i(n_j^2 + n_i n_k)\omega d/c}. \tag{2}$$

The validity of this limit was verified for all the samples studied here. For a thin film in free space ($n_i = n_k = 1$) and in equilibrium ("off", with $n_j = n_{\rm off}$) or after photoexcitation ("on", with $n_j = n_{\rm on}$) we have

$$T_{\rm off,on}(\omega) = \frac{2}{2 - i(n_{\rm off,on}^2 + 1)\omega d/c}. \tag{3}$$

We can work out the relative change in THz spectral amplitude from:

$$\frac{\Delta E}{E} = \frac{E_{\text{on}} - E_{\text{off}}}{E_{\text{off}}} = \frac{T_{\text{on}} - T_{\text{off}}}{T_{\text{off}}} = \frac{T_{\text{on}}}{T_{\text{off}}} - 1, \tag{4}$$

where the second step was made by dividing top and bottom by the reference (no sample) spectrum. Substituting Equations 3 in Equation 4 we have

$$\frac{\Delta E}{E} = \frac{2 - i\left(n_{\text{off}}^2 + 1\right)\omega d/c}{2 - i\left(n_{\text{on}}^2 + 1\right)\omega d/c} - 1. \tag{5}$$

This can be re-arranged to get an expression for $n_{\text{on}}^2 = \epsilon_{\text{on}}$, namely:

$$n_{\text{on}}^2 = \epsilon_{\text{on}} = \frac{n_{\text{off}}^2 + 1 - \frac{2ic}{\omega d}\frac{\Delta E}{E}}{1 + \frac{\Delta E}{E}} - 1. \tag{6}$$

The conductivity of the medium in the photoexcited state can then be worked out from $\sigma_{\text{on}} = -i(\epsilon_{\text{on}} - \epsilon_{\text{lattice}})\omega\epsilon_0$. Alternatively, if there is no change in the lattice dielectric function after photoexcitation, then one can derive $\Delta\sigma = \sigma_{\text{on}} - \sigma_{\text{off}}$ as

$$\Delta\sigma = \frac{-\frac{\Delta E}{E}\left[\frac{2c\epsilon_0}{d} - i\omega\epsilon_0(1 + n_{\text{off}}^2)\right]}{1 + \frac{\Delta E}{E}}. \tag{7}$$

Normally, when the photoexcitation doesn't produce a massive change in the mobility and/or carrier density (i.e. small change in conductivity) then $\Delta E/E$ is small. In this case Equation 6 becomes:

$$n_{\text{on}}^2 = \epsilon_{\text{on}} = n_{\text{off}}^2 - \frac{2ic}{\omega d}\frac{\Delta E}{E} \tag{8}$$

and the standard expression results:

$$\Delta\sigma = -\frac{2c\epsilon_0}{d}\frac{\Delta E}{E} = -\frac{2}{Z_0 d}\frac{\Delta E}{E}. \tag{9}$$

If the first and last medium have refractive index n_i and n_k, then the important equations

(6 and 7) become:

$$n_{\text{on}}^2 = \epsilon_{\text{on}} = \frac{n_{\text{off}}^2 + n_i n_k - \frac{(n_i+n_k)ic}{\omega d}\frac{\Delta E}{E}}{1+\frac{\Delta E}{E}} - n_i n_k, \tag{10}$$

$$\Delta\sigma = -\frac{\Delta E}{E}\left[\frac{(n_i+n_k)c\epsilon_0}{d} - i\omega\epsilon_0(n_i n_k + n_{\text{off}}^2)\right] \Big/ \left(1+\frac{\Delta E}{E}\right). \tag{11}$$

Fitting parameters

The Drude plus plasmon conductivity model used to fit the equilibrium conductivity is given by

$$\sigma(\omega) = \frac{i\sigma_{\text{pl}}\omega\gamma_{\text{pl}}}{\omega^2 - \omega_{\text{pl}}^2 + i\omega\gamma_{\text{pl}}} + \frac{\sigma_D}{1 - i\tau_D\omega}, \tag{12}$$

where σ_D and τ_D are the Drude conductivity and momentum scattering time, and where σ_{pl}, ω_{pl} and γ_{pl} are the plasmon strength, frequency and scattering rate.

This model can describe the conductivity of the film both in equilibrium and at different pump fluences for the pristine sample, as was used to produce the fits in Fig. 1 c) and Fig. 3 a) of the main text. For simplicity the plasmon term was globally fitted, and was assumed not to vary with pump fluence, giving: $\omega_{\text{pl}} = 0.15\,\text{THz}$, $\tau_{\text{pl}} = 1/\gamma_{\text{pl}} = 175\,\text{fs}$ and $\sigma_{\text{pl}} = 2096\,\Omega^{-1}\text{cm}^{-1}$. The Drude term's parameters were allowed to vary at each pump fluence and are reported in Fig. S3. The Drude weight and N_{eff}/m^* behave similarly, as do f_{HWHM} and $1/2\pi\tau_D$. This demonstrates that the model-independent approach used in the main text (based on N_{eff}/m^* and f_{HWHM}) and these detailed fits are in good agreement, and that enhanced fluence lowers the carrier density (or enhances the mass) simultaneously to lowering the momentum scattering rate.

Degradation of a control doped sample

The 30 mM $HAuCl_4$ doped sample was selected as a control sample to investigate potential degradation in the doping efficiency with exposure time in air. The same measurements as described in the main text were taken 5 months after the day when doping was performed.

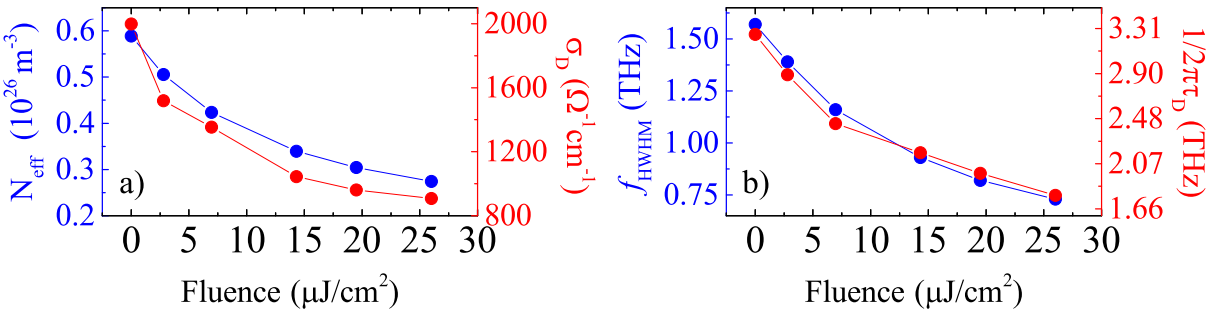

Figure S3: (a) Effective number of electrons, N_{eff} (assuming $m^* = 1$), and DC conductivity σ_D versus fluence, F, (b) frequency width of $\sigma_1(\omega, t = 2\,\text{ps})$, f_{HWHM}, and $1/(2\pi\tau_D)$ using the fitted τ_D from the Drude plus plasmon model, versus F.

For the first month samples were in the glovebox and didn't deteriorate significantly. After 5 months in air a significant change in the properties was observed. Fig. S4 shows that peaks around π plasmon disappeared, and the peak around 1440 nm also disappeared (these peaks were attributed to new intersubband transitions like E_{31} at high doping levels). After 5 months the E_{22} transition was again visible. A new peak at 550 nm was clearly seen, which can be attributed to the plasmon resonance of metallic Au nanoparticles formed from the loss of chlorine. Fig. S4b) shows the change in the Raman spectra. In the aged samples the position of the G^+ mode has shifted back towards its equilibrium position. The conductivity in THz region was also reduced due to the reduction of the doping (Fig. S6). The results reported in the main paper were all obtained on freshly doped samples, stored in nitrogen between experiments.

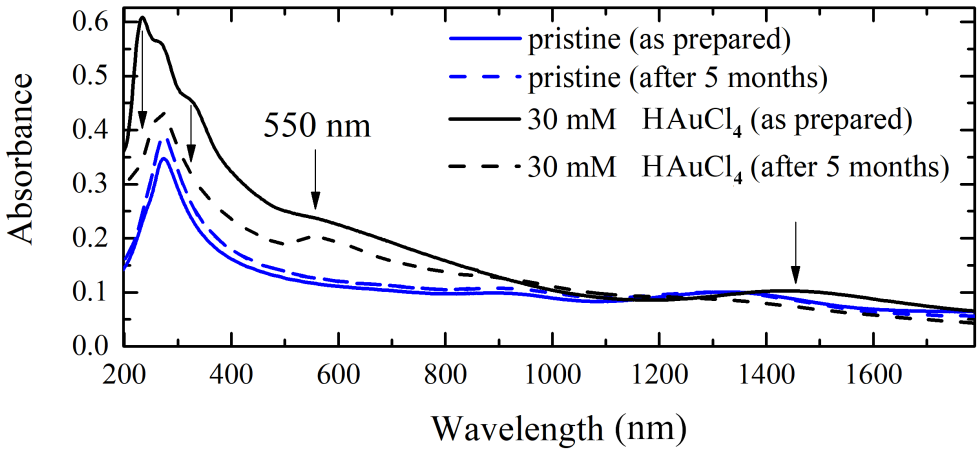

Figure S4: The absorption spectra of pristine (blue) and doped SWCNT with 30 mM $HAuCl_4$ (black) as prepared and after 5 months.

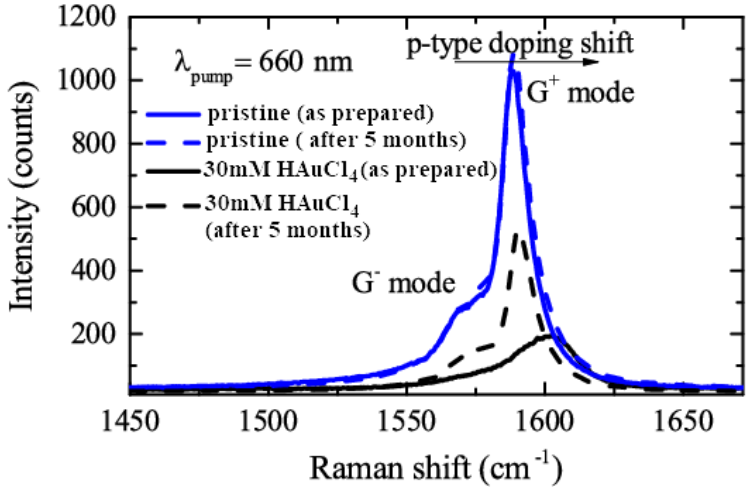

Figure S5: The Raman spectra of pristine (blue) and doped SWCNT with 30 mM $HAuCl_4$ (black) as prepared and after 5 months.

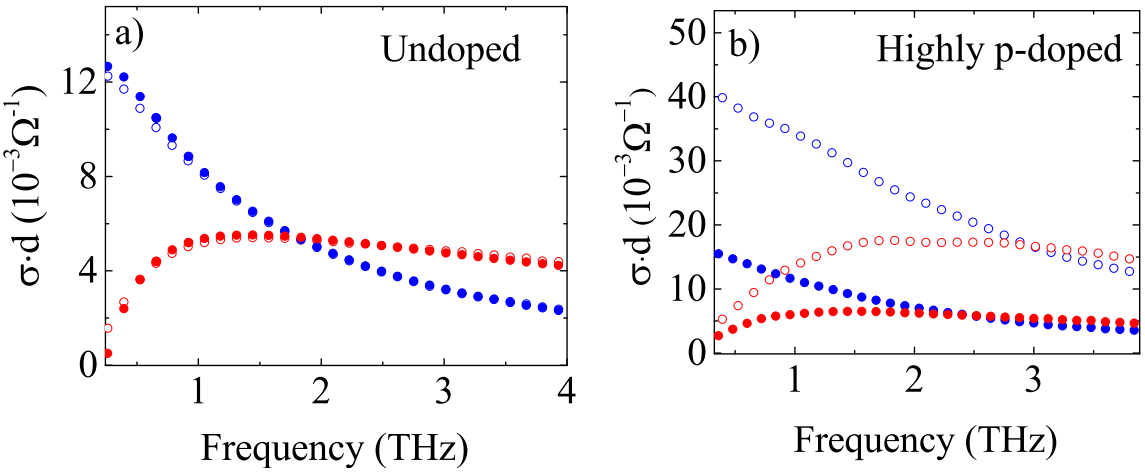

Figure S6: The sheet conductivity of a) pristine and b) doped SWCNT with 30 mM $HAuCl_4$ as prepared (open circles) and after 5 months (filled circles).