Supporting information for: Strong carrier lifetime enhancement in GaAs nanowires coated with semiconducting polymer

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Growth of GaAs nanowires

GaAs NWs were grown on semi-insulating GaAs (111)B substrates with a 50 nm gold-colloid seeded vapor-liquid-solid metal-organic chemical vapor deposition technique. Trimethylgallium and AsH₃ were used as precursors. The NWs were grown via a two-temperature growth procedure to minimize the formation of twin-defects.¹ The growth was initiated with a nucleation step at high

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temperature (450°C) and rapidly ramped down to the subsequent growth temperature (375°C). This procedure yielded GaAs nanowires of core diameter 40–60 nm and of 4–6 μ m in length. The GaAs nanowire side facets are predominantly {112} oriented, resulting in a hexagonal nanowire cross-section.² For control samples discussed below, GaAs/AlGaAs core-shell nanowires were grown for which the GaAs nanowire core was covered by an additional \approx 30 nm-thick layer of AlGaAs. To achieve uniform, conformal deposition of the AlGaAs shells, a high growth temperature (650°C) was used. Full details of the growth procedures have already been reported in Refs. 1 and 3.

XPS measurements and determination of Fermi level at the surface of GaAs NWs

We examined the chemical nature of the surface states present in both as-grown and etched GaAs NWs by performing X-ray photoemission spectroscopy (XPS) measurements at the Daresbury National Centre for Electron Spectroscopy and Surface Analysis. The samples were inserted via a quick-entry load lock into the ultrahigh vacuum (UHV) chamber and kept at a base pressure of $< 10^{-9}$ mbar. The samples were illuminated by 1486.6 eV X-rays generated from a rotating anode Al-K α source filtered by a seven-crystal X-ray monochromator. The photoelectrons emitted along a trajectory 35° off of the surface were collected by a hemispherical analyzer with an energy resolution of 100 meV. Before analyzing the data, a Shirley background was calculated and subtracted from the original spectra.

The Fermi-level (E_F) position near the surface of the GaAs nanowires can be calculated from the X-ray photoemission spectroscopy (XPS) spectra displayed and described in the main manuscript. Here, the Ga_{GaAs} 3d and As_{GaAs} 3d core level regions recorded probe the surface of the wires to a depth of ≈ 2 nm. It has been shown that the binding energy difference between Ga_{GaAs} 3d (As_{GaAs} 3d) and the VBM is 18.8 eV (40.7 eV).⁴ We measured the binding energy of Ga_{GaAs} 3d and As_{GaAs} 3d levels for both as-grown (*o*-GaAs) and etched (*e*-GaAs) nanowires to be 19.3 eV and 41.2 eV respectively (see data in main manuscript). This suggests the E_F position at the nanowire surface is located 0.5 eV above the VBM.

Time-resolved PL spectra of GaAs-NWs and GaAs-NWs/P3HT blends

Figure 1a shows the time-resolved PL spectra collected for *e*-GaAs NWs following excitation at 1.68 eV. At early time after excitation, the spectra are blue-shifted and broadened, compared with the spectra collected at later time delay, due to hot-carrier cooling toward the band edge of GaAs.⁵ Emission spectra collected from the *e*-GaAs NWs/P3HT sample are identical to those collected from bare (uncoated) *e*-GaAs NWs. The PL for the *e*-GaAs NWs/P3HT sample is thus mainly dominated by GaAs NWs and no significant contribution to the photoluminescence originates from P3HT within the spectral region of the GaAs emission ($\approx 1.45-1.57$ eV).



Figure 1: Time-resolved PL spectra of (a) *e*-GaAs NWs and (b) *e*-GaAs NWs/P3HT following excitation at 1.68 eV.

PL emission transient of P3HT

The PL emission collected in the spectral region attributable to the polymer is generally very weak when polymer/NW blends are excited at 1.68 eV as this energy lies below the bandgap of the polymers under investigation. Figure 2 shows the PL emission dynamics for a neat P3HT film and a P3HT/NWs blend film at the emission energy of 1.87 eV, which corresponds to the 0-1 transition in P3HT. We observe PL quenching in the presence of nanowires, which occurs relatively slowly over the first few nanoseconds after excitation. These dynamics are in accordance with two-photon absorption in the polymer, followed by exciton migration and charge separation at the polymer-nanowire interface.



Figure 2: Time-resolved PL recombination of P3HT (blue diamond) and *e*-GaAs NWs/P3HT (red circle) measured at the emission energy of 1.87 eV, following an excitation at energy 1.68 eV. The substrate temperature is held at 10 K. These data were detected with a photomultiplier coupled to a Becker & Hickl time-correlated single photon (TCSPC) card, which gave an overall time resolution of about 200 ps. The inset shows the PL spectrum of a P3HT film excited at an energy of 3.1 eV. The red arrow indicates the energy at which the time-resolved PL was probed.

PL transients of e-GaAs NWs and e-GaAs NWs/F8BT

For a control experiment, we fabricated hybrid type-I heterojunction films by blending *e*-GaAs NWs with F8BT. In this case, charge-injection from GaAs NWs into F8BT should be blocked by the higher bandgap and type-I band alignment with respect to F8BT (see main manuscript). Figure 3 shows the transient PL decay traces of *e*-GaAs NWs and *e*-GaAs NWs/F8BT film samples. The initial slow rise observed in *e*-GaAs NWs/F8BT can be attributed to the ultrafast energy transfer from F8BT to the nanowires owing to its higher bandgap. However, the long-term emission rate of *e*-GaAs NWs in the F8BT matrix is similar to that in the bare (uncoated) *e*-GaAs NWs. This suggests that in presence of an F8BT overcoat, charge-carrier recombination is still dominated by ultrafast trapping at surface defect states.



Figure 3: Transient PL decay traces of *e*-GaAs NWs and *e*-GaAs NWs/F8BT following excitation at an energy of 1.68 eV at 10 K. The PL transients are measured at the emission energy of 1.52 eV, which corresponds to the bandgap of the GaAs NWs.

PL transients for core-shell GaAs/AlGaAs NWs with and with-

out P3HT coating



Figure 4: Transient PL decay traces of core-shell GaAs/AlGaAs NWs and GaAs/AlGaAs NWs/P3HT following excitation at 1.68 eV, measured at 10 K. The PL is detected at an emission energy of 1.52 eV, which corresponds to the bandgap of GaAs.

As a further control experiment Figure 4 shows the transient PL of GaAs NWs overcoated with a 30 nm-thick AlGaAs layer in the absence (GaAs/AlGaAs NWs) and presence (GaAs/AlGaAs NWs/P3HT) of a P3HT overcoat. The PL decay rate remains unchanged upon coating these coreshell nanowires with P3HT, i.e. the carrier trapping in GaAs/AlGaAs NWs is not affected by the presence of the polymer. The thick overcoat of AlGaAs hence appears to suppress charge doping and surface passivation by the polymer, as well as any photoinduced charge separation.

Modeling a GaAs/P3HT interface via density-functional theory

DFT calculations within the local-density approximation (LDA)⁶ were performed using the Quantum ESPRESSO software package.⁷ Ultrasoft⁸ (H, C, S) and norm-conserving⁹ (Ga, As) pseudopotentials were used to account for the core-valence interaction. Valence electronic wavefunctions and charge density were described using plane wave basis sets with kinetic energy cutoffs of 70 Ry and 350 Ry, respectively. The lattice parameters of bulk wurtzite GaAs were optimized using a $8 \times 8 \times 8$ Brillouin Zone (BZ) grid, yielding values (a=3.99 Å, c=6.58 Å) in agreement with experiment¹⁰ and theory.¹¹ The sructure of bulk P3HT was optimized as described in Ref. 12. Structural relaxations of the interface were carried out with sampling of the BZ at the Γ point.

GaAs nanowires exhibit both zinc blende and wurtzite structures.^{10,13,14} Since the wurtzite $(10\overline{1}0)$ surface is crystallographically parallel to the zinc blende {112} face, it is therefore comparable and we choose to model the GaAs/P3HT interface using a wurtzite GaAs($10\overline{1}0$) surface, using a conformation similar to our previous work on the related ZnO/P3HT interface.¹² The atomistic model of the GaAs/P3HT interface consists of 428 atoms. Four layers of GaAs were used, with the bottom two layers held fixed in order to mimic bulk GaAs. All other atoms were allowed to relax. The transverse area of the GaAs slab is 15.96 Å, × 13.16 Å, and periodic images of the slabs were separated by 8 Å of vacuum.

The electronic charge redistribution upon formation of the interface was determined by calculating $\Delta n(\mathbf{r}) = n_{\text{GaAs/P3HT}}(\mathbf{r}) - [n_{\text{GaAs}}(\mathbf{r}) + n_{\text{P3HT}}(\mathbf{r})]$. In this expression \mathbf{r} represents the position vector within the computational cell, $n_{\text{GaAs/P3HT}}$ the ground state charge density of the GaAs/P3HT interface, n_{GaAs} the charge density of the GaAs slab without the P3HT layers in the same computational cell, and n_{P3HT} the charge density of the P3HT layers without the GaAs slab. The electrostatic potential offset is calculated by integrating, using Poisson's equation, the planar average charge of $\Delta n(\mathbf{r})$ from the middle of the GaAs slab to the middle of P3HT layer.

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