

## Electronic Supplementary Information

### **Mixed-ligand-functionalized Silicon-germanium Alloy Nanocrystals with Improved Carrier Mobilities**

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## Experimental Section

**Materials.** All chemicals used are commercially available and were used without any additional purification steps. Triethoxysilane (TriEOS, 95%), hydrofluoric acid (HF, 49% aqueous solution, electronic grade), toluene (99%), oleylamine (OAm, 90%), 1-octadecene (ODE, 90%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ , 30 wt.% in  $\text{H}_2\text{O}$ ), and potassium hydroxide (KOH, 95%) were purchased from Aladdin Inc. Tetraethoxygermane (TEOG, 97%) was purchased from Gelest Inc. Ethanol (EtOH, 99.7%) was purchased from Energy chemical Inc. Methanol (MeOH,  $\geq 98\%$ ) was purchased from Guangzhou Sci-Tech Co., Ltd. Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS, 1.3-1.7 wt.% dispersion in  $\text{H}_2\text{O}$ ), 1,3,5-Tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi,  $>99.9\%$ ), and 4,4'-Bis(N-carbazolyl)-1,1'-biphenyl (CBP,  $>99.9\%$ ) were purchased from Xi'an Yuri Solar Co., Ltd. Lithium fluoride ( $\text{LiF}$ ,  $\geq 99.98\%$ ) was purchased from Sigma-Aldrich Inc. Molybdenum trioxide ( $\text{MoO}_3$ , 99.99%), aluminium (Al, 99.99%) and silver (Ag, 99.99%) were purchased from China New Metal Materials Technology Co., Ltd. Zinc acetate dihydrate ( $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ , 99.995%) was purchased from Shanghai Macklin Biochemical Co., Ltd. Indium tin oxide (ITO) substrates ( $1.5 \times 1.5 \text{ cm}^2$ ) were purchased from Ying Kou Shang Neng Photoelectric Materials Co., Ltd.

**Solid-state synthesis of silicon-germanium (SiGe) alloy nanocrystals (NCs).** 15 ml of MeOH was mixed with 12.6 ml of TriEOS (64.9 mmol) and 0.75 ml of TEOG (3.3 mmol) in a 100-ml Schlenk flask with magnetic stirring for 30 min under a nitrogen atmosphere at room temperature to form a homogenous solution. After that, 10 ml of diluted  $\text{HNO}_3$  aqueous solution (0.3 M) was drop wisely injected into the solution to initiate the catalytic hydrolysis and condensation reactions under a nitrogen atmosphere. The transparent, colorless solution

immediately turned cloudy and a considerable amount of purple-red gel-like product gradually formed. The mixture was then set still under a nitrogen atmosphere for 24 h. After the aging process, the gel-like product was isolated and washed with 15 ml of anhydrous methanol for 3 times, and subsequently dried under vacuum at 40°C for 24 h. The dried product was ground using an agate mortar and pestle, yielding deep red powders. ~1 g of the powders was placed in a quartz reaction boat and transferred to a high-temperature tube furnace (Lindberg). The sample was heated from ambient to 1100°C at 18°C/min in a slightly reducing atmosphere (95% Ar + 5% H<sub>2</sub>) and maintained at the processing temperature for 1 h. After that, the sample was naturally cooled down under continuous gas flow to room temperature. The resulting grey-brown powdery product was ground to fine powders and stored in a 20-ml vial in ambient condition for further use.

**Liberation of SiGe NCs.** An optimized two-step etching process was applied to liberate the alloy particles from the oxide matrix.<sup>1-2</sup> ~0.9 g of the grey-brown fine powder was transferred to a 100-ml of beaker. 30 ml of water and 30 ml of H<sub>2</sub>O<sub>2</sub> (30 wt.%, aqueous solution) were added to the beaker and stirred vigorously for 30 min to remove the bulk Ge crystals. The resulting brown powder was separated using centrifugation at 7800 rpm for 5 min, isolated from the mixed solution, and washed with water and ethanol. The purified powders were then dried under vacuum for 24 h. Next, ~0.3 g of the dried H<sub>2</sub>O<sub>2</sub>-etched product was transferred to a polyethylene terephthalate beaker equipped with a Teflon-coated stir bar. 4.5 ml of deionized water and 4.5 ml of ethanol were added to the beaker with mechanical stirring to form a grey-brown suspension. 4.5 ml of 49%-51% HF aqueous solution was subsequently added into the mixture in ambient conditions under mechanical stirring to initiate the etching reaction (Caution! HF

solution must be handled with extreme care). After 1 h, the color of the suspension gradually changed to grey. ~50 ml of toluene was added to extract the hydride-terminated SiGe NCs and then transferred to 50 ml centrifuge tube. The NCs were precipitated through centrifugation at 7800 rpm for 10 min and further dispersed in 10 ml of toluene for another round of centrifugation at 7800 rpm for 10 min. The precipitates after two cycles of centrifugation were dispersed in 2 ml toluene for further functionalization.

**Surface of SiGe NCs with 1-octadecene (ODE).** 10 ml of ODE (28.2 mmol) and 1 mg of the radical initiator azobisisobutyronitrile (AIBN, 6  $\mu$ mol) were transferred to a 100-ml Schlenk flask with vigorous mechanical stirring under vacuum at 65°C for 15 min until the AIBN was completely solved. After that, the flask was refilled with nitrogen. Under constant nitrogen flow, 2 ml of the abovementioned hydride-terminated SiGe NCs toluene solution was quickly injected into the flask to initiate the surface functionalization. The reaction was maintained at 65°C for over 12 h under nitrogen atmosphere. After the reaction, the flask was naturally cooled down to room temperature. The product solution was concentrated using rotary evaporation at 40°C and only ~10 ml of the solution remained. The concentrated solution was obtained and further transferred to two centrifuge tubes. ~30 ml of methanol/ethanol mixed solution (1:1 volume ratio) was added to centrifuge tube to yield cloudy dispersion. The tubes were then centrifuged at 7800 rpm for 15 min. After centrifugation, the supernatant was decanted, and the NCs were redispersed in ~0.5 ml of octane for further devices fabrication.

**Surface functionalization of SiGe NCs with oleylamine (OAm).** 10.3 ml of OAm (28.2 mmol) was transferred to a 100-ml Schlenk flask with vigorous mechanical stirring under vacuum at 60°C for 15 min. After that, the flask was refilled with nitrogen gas. Under constant nitrogen flow, 2

ml of the abovementioned hydride-terminated SiGe NCs toluene solution was quickly injected into the flask to initiate the surface functionalization. The functionalization reaction was maintained at 65°C for 1-3 h under nitrogen atmosphere to yield a transparent orange solution. After the reaction, the flask was naturally cooled down to room temperature. The product solution was concentrated using rotary evaporation at 40°C and only ~10 ml of the solution remained. The concentrated solution was obtained and further transferred to two centrifuge tubes. ~30 ml of methanol/ ethyl acetate mixed solution (1:1 volume ratio) was added to centrifuge tube to yield cloudy dispersion. The tubes were then centrifuged at 7800 rpm for 15 min. After centrifugation, the supernatant was decanted, and the NCs were redispersed in ~2 ml of toluene or octane for further use.

**Two-step surface functionalization of SiGe NCs using ODE and OAm.** 10 ml of ODE (28.2 mmol) and 1 mg of AIBN (6  $\mu$ mol) were added to a 100-ml Schlenk flask with vigorous mechanical stirring under vacuum at 65°C for 15 min until the AIBN was completely solved. After that, the flask was refilled with nitrogen gas. Under constant nitrogen flow, ~2 ml of the abovementioned hydride-terminated SiGe NCs toluene solution was quickly injected into the flask to initiate the surface functionalization. The functionalization reaction was maintained at 65°C for over 12 h under nitrogen atmosphere. After that, 5.1 ml of OAm (14.1 mmol) was injected into the flask to initiate the second step functionalization at 65°C. After 3 h, the flask was naturally cooled down to room temperature. The product solution was concentrated using rotary evaporation at 40°C and only ~15 ml of the solution remained. The concentrated solution was further transferred to two 50-ml centrifuge tubes. ~30 ml of methanol/ethyl acetate mixed solution (1:1 volume ratio) was added to centrifuge tube to yield cloudy dispersion. The tubes were then centrifuged at 7800

rpm for 15 min. After centrifugation, the supernatant was decanted, and the NCs were redispersed in ~0.5 ml of octane for further devices fabrication.

**Synthesis of colloidal ZnO NCs:** ZnO NCs were prepared using previously developed method.<sup>3</sup> Briefly, a 200-ml Schlenk flask was heated to 64°C in an oil bath, then a solution mixture containing 3.53 g of zinc acetate dihydrate ( $\text{Zn}(\text{Ac})_2 \cdot 2\text{H}_2\text{O}$ , 16.1 mmol) and 125 ml of MeOH was added into a flask with magnetic stirring. The stirring was kept at 64°C for 10 min. 1.48 g of potassium hydroxide (KOH, 26.4 mmol) was completely dissolved into 65 ml of MeOH at room temperature to form a homogenous solution. The solution was then added dropwise into the flask with magnetic stirring, and the process was completed within 1 h. The reaction was immediately initiated proceed at 64°C for 2 h. After that, the flask was cooled down to room temperature and kept still for the self-precipitation of the NCs. After 3 h, the supernatant was decanted and 50 ml of MeOH was added into the flask to form a milky solution. The mixed solution was evenly distributed into two 50-ml centrifuge tubes and centrifugated at 2500 rpm for 3 min. After that, the supernatant was decanted and 50 ml of clean MeOH was added into the centrifuge tubes to form homogenous suspension. The tubes were then centrifuged at 6000 rpm for 2 min. The supernatant was decanted and the product ZnO NCs was redispersed in 10 ml of clean chloroform. Additional 10 ml of clean MeOH was added to make a homogeneous ZnO solution with a concentration of 40-50 mg/ml. The solution was stored in a nitrogen-filled glovebox for further use.

**Fabrication of the hole- and electron-only devices:** For the fabrication of electron-only devices, the indium tin oxide (ITO) substrates were cleaned by multiple times of washing using detergent, deionized water, ethanol, acetone, and isopropyl alcohol under sonication for 30 min

for each step. The clean substrates were then dried under continuous N<sub>2</sub> flow and processed with ultraviolet/ozone treatment at 80 W for 15 min prior to the use. ~80 μl of the abovementioned ZnO NC solution was firstly spin-coated on the clean ITO substrate at 3000 rpm for 40 s. Subsequently, 45 μl of SiGe/octane solution (50 mg/ml of ODE-capped and 66 mg/ml of ML-capped) was spin-cast on the substrate at 2000 rpm for 40 s in the nitrogen-filled glovebox, followed by thermal annealing at 200°C for 30 min. The thin films were then cooled down to room temperature. 35 nm of TPBi, 1 nm of LiF, and 100 nm of Al were thermally deposited on the thin films to complete the devices.

As for the fabrication of hole-only devices, the ITO substrates were treated using the same procedure as the mentioned in the section of the fabrication of the electron-only devices. ~80 μl of PEDOT:PSS aqueous solution (1.3-1.7 wt.% dispersion in H<sub>2</sub>O) was firstly spin-coated on clean ITO substrates at 4000 rpm for 40 s under ambient conditions, followed by thermal annealing at 150°C for 30 min and naturally cooling down to room temperature. Subsequently, the ITO/PEDOT:PSS films were transferred into a nitrogen-filled glovebox. 45 μl of SiGe/octane solution (50 mg/ml of ODE-capped and 66 mg/ml of ML-capped SiGe NCs) was spin-cast on the substrate at 2000 rpm for 40 s, followed by thermal annealing at 200°C for 30 min. The thin films were then cooled down to room temperature. 60 nm of CBP, 6 nm of MoO<sub>3</sub>, and 100 nm of Ag were thermally deposited on the thin films to complete the devices.

Each ITO substrate was patterned to yield 4 devices for both device architectures, each with an active area of 8 mm<sup>2</sup>.

**Determination of carrier mobility and trap density values from space-charge-limited current (SCLC) measurements:** the device architectures were ITO/PEDOT:PSS (80 nm)/ SiGe NCs film (180-190 nm)/CBP (60 nm)/MoOx (6 nm)/Ag (120 nm) and ITO/ZnO (40nm)/ SiGe NCs film (180-190 nm)/TPBi (35 nm)/LiF (1 nm)/Al (110 nm) for the hole-only and electron-only devices, respectively. The carrier mobility values were calculated using Mott-Gurney's equation:

$$\mu = \frac{8J_D d^3}{9\varepsilon\varepsilon_0 V^2} \text{ (Equation 1)}$$

where  $J_D$  is the current density,  $d$  is the thickness of SiGe NCs thin film,  $\varepsilon_0$  and  $\varepsilon$  are the vacuum permittivity and relative permittivity. The value used for mobility calculation is  $d = 180\text{-}190$  nm (obtained from the device cross-sectional image, Figure S3 and S4), and  $\varepsilon = 13.95$  for crystalline Ge.<sup>4-5</sup>

The values of the trap densities for electron and hole are calculated using the following equation:

$$n_{t(e/h)} = \frac{2\varepsilon\varepsilon_0 V_{TFL(e/h)}}{ed^2} \text{ (Equation 2)}$$

where  $n_{t(e/h)}$  is the trap state density,  $V_{TFL}$  is the trap-filled limit voltage, and  $e$  is the elementary charge.

**Devices Performance Characterizations.** The characterizations were carried out at room temperature in a nitrogen-filled glovebox. Current density-voltage ( $J$ - $V$ ) characteristics were recorded by Keithley 2400 source meter with a step of 0.05 V (19 ms for each step). The active device area was 0.08 cm<sup>2</sup>.



**Transmission electron microscopy (TEM) studies.** The TEM imaging was performed using an FEI Talos F200s electron microscope with an accelerating voltage of 200 kV. The functionalized SiGe NCs were redispersed in toluene, then drop-cast onto a piece of 200-mesh carbon-coated copper TEM grid. The TEM grid was dried in a vacuum oven at 25°C for 16 h to remove the residual solvent prior to the imaging. All images were processed using ImageJ (software version: ImageJ 1.52a).

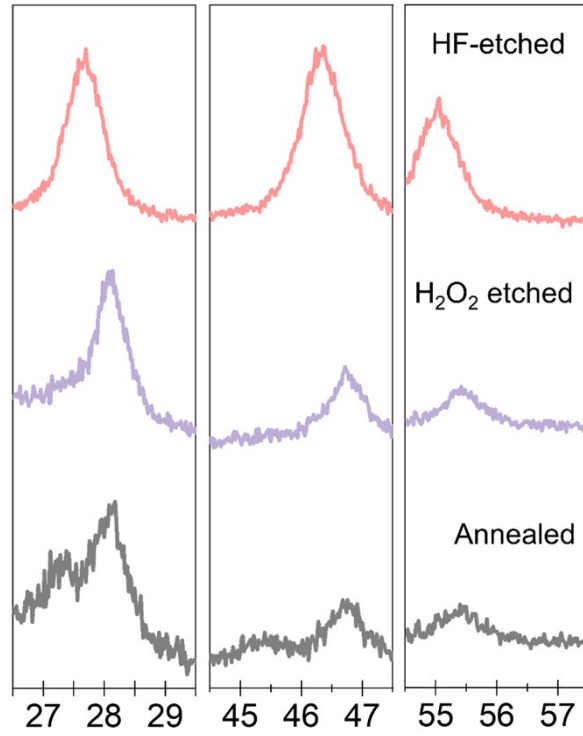
**Static-state photoluminescence studies.** All of the excitation-emission matrix (EEM) spectra and static-state PL results of the NC samples were obtained using an FLS1000 fluorescence spectrometer equipped with a Xenon lamp with a monochromator (Edinburgh Instruments). The PL lifetime decay results were acquired with a 365 nm pulse laser excitation from a picosecond pulsed diode laser station (Edinburgh Instrument Ltd., EPL 365 nm). The absorption spectra were recorded using a UV3600 fluorometer (Shimadzu Inc.).

**Powdery X-ray diffraction (PXRD) measurements.** The PXRD patterns were measured using a Rigaku Miniflex 600 diffractometer (Cu-K $\alpha$ ,  $\lambda = 1.5406 \text{ \AA}$ ) operating at a voltage of 45 kV and a current of 15 mA.

**Fourier-transform infrared (FT-IR) and Raman spectroscopic measurements.** The functionalized SiGe NCs were extracted from the toluene solution through the antisolvent approach. 6 ml of MeOH was added to the SiGe NC/toluene solution to precipitate the NC and the solid was isolated from the solution by the centrifugation at 7800 rpm for 10 min. The supernatant was decanted, and the precipitate was transferred to a 20-mL vial and dried in a vacuum oven at 40°C overnight. The dried solid was transferred onto the the diamond sample window on the Nicolet/Nexus-670 FT-IR spectrometer (ATR mode) for the FT-IR measurements

As for the Raman study, The NC samples were precipitated and dried in a vacuum oven at 40°C overnight. The dried powders were transferred onto the sample window of the TriVista 557, Princeton Instruments for Raman characterization. The laser wavelength of 532 nm with 1 mW of power were used as the excitation source.

**XPS measurements.** XPS measurements were carried out using a Thermo Scientific KAlpha XPS system with a monochromatic Al K $\alpha$  X-ray source (1486.7 eV, spot size: 400  $\mu$ m). The electron kinetic energy was measured by an energy analyzer operated in the constant analyzer energy mode at 100 eV for elemental spectra. All spectra were internally calibrated to the C 1s emission (284.8 eV). Casa XPS software (ver. V2.3.16.PR1.6, VAMAS) was used to analyze the data.



**Fig. S1.** Zoom-in XRD patterns of the c-Ge/SiGe NC/GSO composites before and after H<sub>2</sub>O<sub>2</sub> and HF etching processes.

**Note S1. Calculation details of the Si:Ge ratio in SiGe-containing composites.**

In this study, we applied a modified version of Vegard's Law for SiGe alloy particles:

$$a(x) = (0.002733x^2 + 0.01992x + 0.5431) \text{ nm (Equation 3)}$$

where  $a$  = lattice constant, and  $x$  = Ge content ( $0 \leq x \leq 1$ ).

The lattice constant  $a$  is calculated according to the following Equation 2 and Equation 3:

$$2d_{(hkl)}\sin\theta = n\lambda \text{ (Equation 4)}$$

**Equation 2** is the Bragg's equation for the calculation of  $d_{(hkl)}$ , where  $n = 1$ ,  $\lambda = 0.15406$  nm,  $\theta$  represents the angle between reflected rays and crystal planes.  $\theta$  was obtained from the XRD result.  $d_{(hkl)}$  represents the interplanar crystal spacing.

$$\frac{1}{d_{(hkl)}} = \frac{\sqrt{h^2 + k^2 + l^2}}{a} \text{ (Equation 5)}$$

**Equation 3.** The calculation of lattice constant  $a$  according to the calculated  $d_{(hkl)}$ , where  $a$ =lattice constant,  $(hkl)$  represents Miller index.

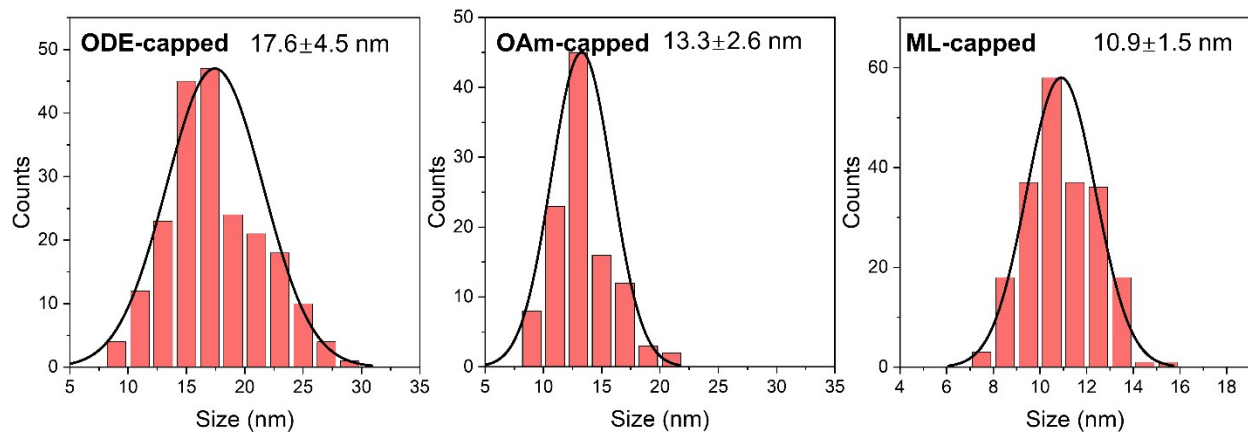
All calculated results were summarized in Table S1 and Table S2 as shown below.

**Table S1.** Summary of the calculated results of interplanar crystal spacing, lattice constant and Ge content (i.e., the value  $x$ ) of the sample after HF etching.

<b>(hkl)</b>	<b><math>d</math> (nm)</b>	<b><math>a</math> (nm)</b>	<b><math>x</math></b>
(111)	0.321	0.555	0.54
(220)	0.196	0.554	0.51
(311)	0.167	0.553	0.48

**Table S2.** Summary of the calculated results of interplanar crystal spacing, lattice constant and Ge content (i.e., the value  $x$ ) of the sample after  $H_2O_2$  etching.

<b>(hkl)</b>	<b><math>d</math> (nm)</b>	<b><math>a</math> (nm)</b>	<b><math>x</math></b>
(111)	0.317	0.550	0.31
(220)	0.194	0.550	0.31
(311)	0.166	0.549	0.30



**Fig. S2.** Electron microscopic study of SiGe NCs capped with various types of ligands: the size distribution analyses of ODE-capped, OAm-capped and ML-capped SiGe NCs.

**Note S2. Details of the data analysis of the PL lifetime decay in Figure 3**

All time-resolved PL decay results shown in Figure 3c and 3d were fitted using the following equation:

$$y(t) = y_0 + A_1 e^{-(x-x_0)/\tau_1} + A_2 e^{-(x-x_0)/\tau_2} + \dots + A_n e^{-(x-x_0)/\tau_n} \quad (\text{Equation 4})$$

The average lifetime results were calculated using the intensity-weighted model as

$$\tau_{\text{ave}} = \frac{A_1 \tau_1^2 + A_2 \tau_2^2 + A_3 \tau_3^2 + \dots + A_n \tau_n^2}{A_1 \tau_1 + A_2 \tau_2 + A_3 \tau_3 + \dots + A_n \tau_n} \quad (\text{Equation 5})$$

All fitted results were summarized in Table S3 and Table S4 as shown below.

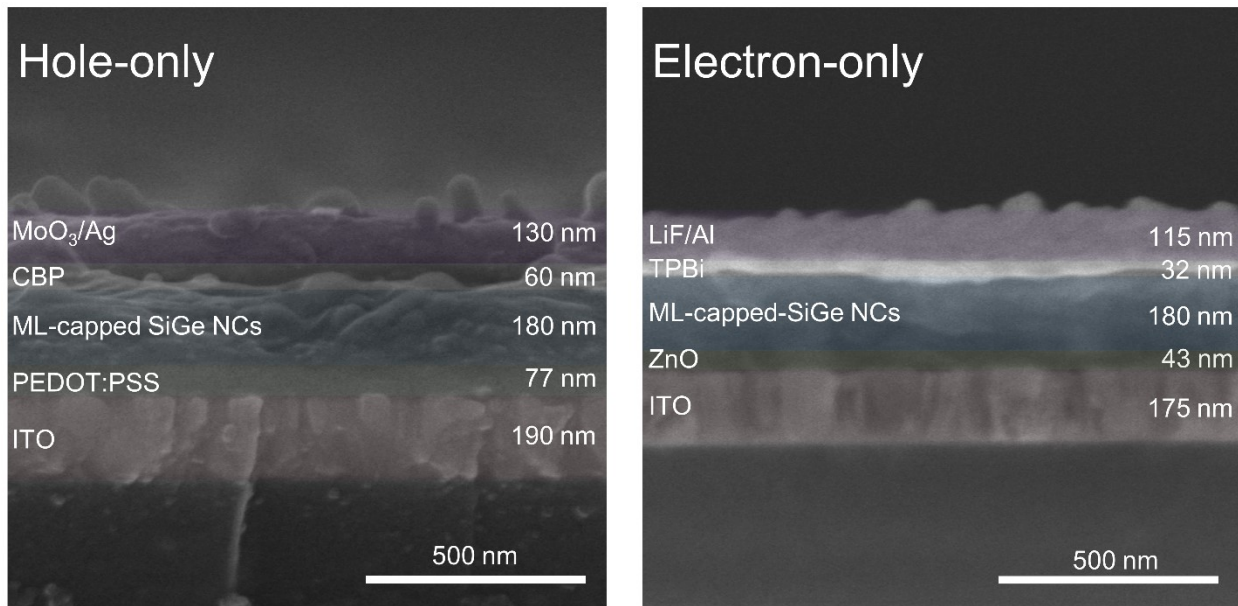
**Table S3.** Summary of the fitting results of the lifetime decay values of the ODE-capped, OAm-capped and ODE/OAm co-passivated SiGe NCs (emission wavelength: 407-437 nm).

	Emission (nm)	$\tau_1$ (ns)	$\tau_2$ (ns)	$\tau_3$ (ns)	$\tau_{ave}$ (ns)
ODE-capped	437	1.25 (80.82%)	4.76 (19.18%)	NA	1.92
OAm-capped	407	0.42 (69.78%)	4.31 (30.22%)	NA	1.60
ODE/OAm co-passivated	427	0.96 (70.05%)	4.60 (29.95%)	NA	2.05

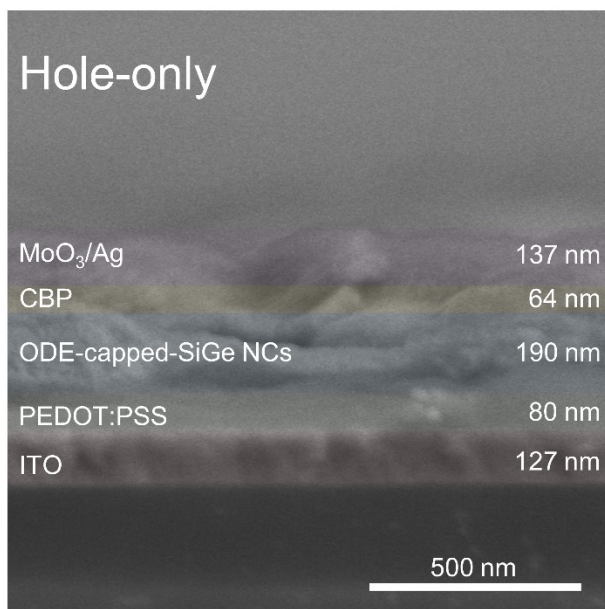
**Table S4.** Summary of the fitting results of the lifetime decay values of the ODE-capped ODE/OAm co-passivated SiGe NCs (emission wavelength: 763-779 nm). OAm-capped SiGe NCs have no NIR PL.

	Emission (nm)	$\tau_1$ ( $\mu$ s)	$\tau_2$ ( $\mu$ s)	$\tau_3$ ( $\mu$ s)	$\tau_{ave}$ ( $\mu$ s)
ODE-capped	779	5.35 (10.38%)	29.47 (42.75%)	97.83 (46.86%)	59.00
ODE/OAm co-passivated	763	7.27 (7.58%)	34.06 (51.51%)	99.92 (40.91%)	58.98

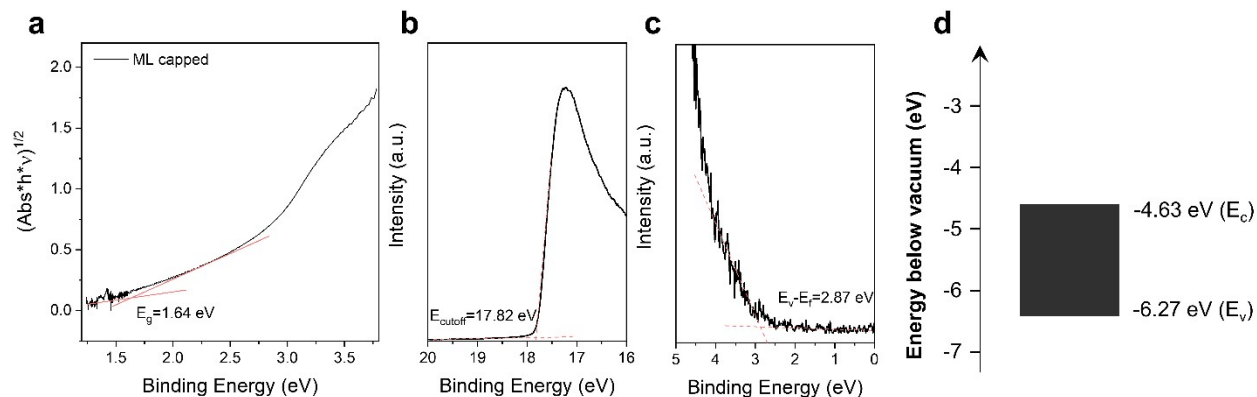




**Fig. S3** Hole-only and electron-only devices cross-sectional SEM images of ML-capped SiGe NC

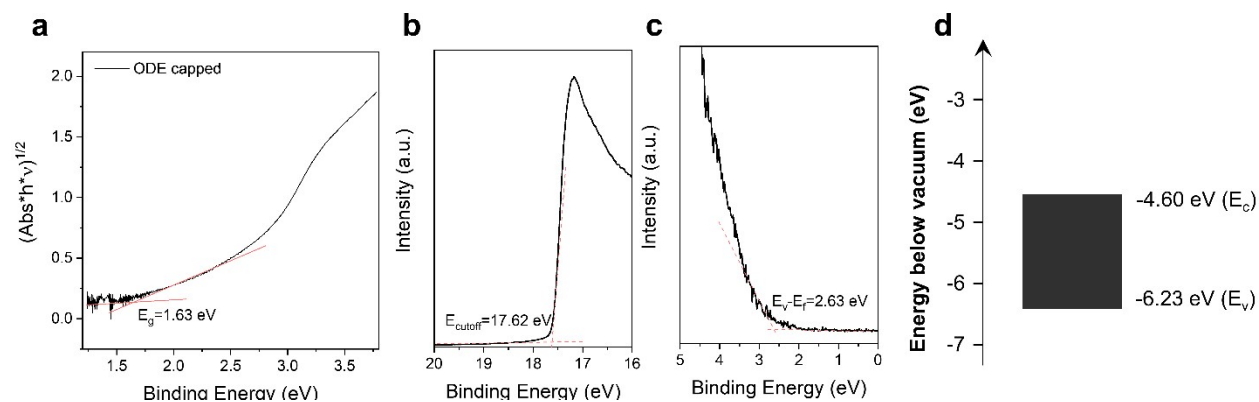


**Fig. S4** Hole-only device cross-sectional SEM images of ODE-capped SiGe NC



**Fig. S5** (a) The Kubelka–Munk equation applied to the absorbance spectrum. (b-c) UPS spectra.

(d) Scheme of the energy band alignment of the ML-capped SiGe NCs



**Fig. S6.** (a) The Kubelka–Munk equation applied to the absorbance spectrum. (b-c) UPS spectra.

(d) Scheme of the energy band alignment of the ODE-capped SiGe NCs.

**Table S5.** carrier mobilities and trap densities from SCLC analysis.

	$\mu_e$ (cm <sup>2</sup> V <sup>-1</sup> S <sup>-1</sup> )	$\mu_h$ (cm <sup>2</sup> V <sup>-1</sup> S <sup>-1</sup> )	$n_{te}$ (cm <sup>-3</sup> )	$n_{th}$ (cm <sup>-3</sup> )
ODE-capped	$5.4 \cdot 10^{-6}$	$4.9 \cdot 10^{-7}$	$6.8 \cdot 10^{16}$	$2.3 \cdot 10^{17}$
ML-capped	$6.3 \cdot 10^{-6}$	$1.1 \cdot 10^{-6}$	$5.2 \cdot 10^{16}$	$6.2 \cdot 10^{16}$

## References

1. M. Javadi, V. K. Michaelis and J. G. C. Veinot, *J. Phys. Chem. C* 2018, **122**, 30, 17518-17525.
2. E. J. Henderson, M. Seino, D. P. Puzzo and G. A. Ozin, *ACS Nano* 2010, **4**, 12, 7683-7691.
3. B. Sun and H. Siringhaus, *Nano Lett.* 2005, **5**, 12, 2408-13.
4. I. D. Avdeev, A. V. Belolipetsky, N. N. Ha, M. O. Nestoklon and I. N. Yassievich, *J. Appl. Phys.* 2020, **127**, 11.
5. L. F. Mao, C. Y. Zhu, L. J. Zhang, A. M. Ji and X. Y. Liu, *Current Nanoscience* 2013, **9**, 1, 103-106.