Graphene-templated directional growth of an inorganic nanowire

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Supplementary Text

Elemental analysis We analyse the nanowire samples using energy dispersive x-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS). In this elemental analysis, we focus on the elements of C, N, O, S, (H), and Au, which the precursor solution contains. The EDX spectra with/without the nanowires (Supplementary Fig. 5a, b) indicate the presence of Au within the nanowires. We also confirm that Au is localized in the nanowires using EDX chemical mapping (Supplementary Fig. 5c, d). Using EDX for identifying other light elements is not appropriate because e-beam irradiation decomposes the nanowire material (Fig. 4h–j and Supplementary Video 1) and light elements (C, H, O, and S) are lost during the long measurement time of EDX (in our case, 30 sec with an electron voltage of 100 kV). EELS has better sensitivity for observation of light elements and can reduce the measurement time (in our case, 0.2 sec × 5 times with an electron voltage of 80 kV), thus allows us to further identify those elements from our nanowires. The EELS spectra with/without the nanowires (Supplementary Fig. 6a–d) show the presence of N within the nanowires in the repeated measurements. The peaks for O and S from the precursor solution are not present in the nanowires. We additionally confirm that N is localized in the nanowires using energy-

filtered TEM imaging at N K-edge (Supplementary Fig. 6e, f). Taken together, our EDX and EELS results indicate that the nanowires contain Au and N with the possible presence of C and/or H.

In addition, characteristic features of the measured EELS carbon peaks should be noted. The energy loss region at the C 1s (K edge) consists of two peaks – a sharp peak near 285 eV due to excitation to π* states and a broad peak over 290 eV due to excitation to σ* states[34]. While the sample areas without nanowires (Supplementary Fig. 6b, c) show typical EELS spectra of graphene, the EELS carbon spectrum from the nanowires (Supplementary Fig. 6a) shows different characteristics; the height ratio of the π* peak to the σ* peak is larger than that of graphene. This feature suggests that the nanowires have the increased number of π-bonded electrons compared to graphene (sp^2 bonded carbons), thus indicating the possible presence of sp^1 bonded carbons in the nanowires. This observation is consistent with the sp^1 electronic state of carbon atoms in AuCN.

Supplementary Methods

Graphene preparation Graphene is synthesized by chemical vapour deposition (CVD) on 25 μm thick copper foil (99.8 %, Alfa Aesar, Ward Hill, MA). The copper foil is inserted into a quartz tube and heated to 1,000 °C under a H_2 flow of 10 sccm at 150 mTorr. After annealing for 30 min, a gas mixture of 25 sccm CH_4 and 10 sccm H_2 at 520 mTorr is introduced for 20 min to synthesize graphene. Finally, fast cooling to room temperature with a CH_4 flow of 20 sccm under a pressure of 330 mTorr is performed. Graphene samples purchased from Graphene Platform, Inc. are also tested. For the nanowire synthesis experiments shown in Supplementary Fig. 9f-h, sub-monolayer graphene samples are used. The 25 sccm CH_4 flow is introduced only for 1 min during graphene growth.

Au nanoparticle preparation Two types of Au nanoparticles are used in this study: spherical Au nanoparticles (diameter: 8 nm) dispersed in toluene and Au nanorods (diameter: 25 nm, length: 73

nm, purchased from Nanopartz Inc.) dispersed in ethanol. The spherical Au nanoparticles are prepared by the following synthetic method, as previously reported[35], with modifications. Required chemicals: Gold chloride (AuCl$_3$, 99 %, Aldrich), didodecyldimethylammonium bromide (DDAB, Fluka), sodium borohydride (NaBH$_4$, 99.99 %, Aldrich), and dodecanethiol (DDTh, > 98 %, Aldrich) are purchased and used without further purification. 51 mg of gold chloride and 0.173 g of DDAB are dissolved by sonication in 15 mL toluene. A total of 54 μL of 9.4 M NaBH$_4$ aqueous solution is added dropwise to the reaction flask while stirring the solution at room temperature. Red-coloured gold colloids form after 20 min. A 1.5 mL aliquot of DDTh is added to the gold colloids for ligand exchange. The gold nanocrystals are then precipitated with ethanol, vacuum-dried, and re-dissolved into 45 mL of toluene. Another 4.5 mL of DDTh is added, and the solution is heated under reflux for 12 hour. Gold nanocrystals are precipitated with acetone and re-dispersed in toluene. This solution is further filtered with qualitative grade filter paper to remove any aggregated gold colloids. The gold nanocrystals are re-dispersed in 5 mL toluene and maintain colloidal stability for several months. The gold nanoparticles are diluted with toluene to desired concentration for nanowire synthesis (for typical experiments, a 1/10 dilution factor is used).

Nanowire synthesis The nanowire synthesis on graphene is performed with different types of gold precursors: (i) spherical gold nanoparticles, (ii) gold nanorods, and (iii) a gold grid mesh (Supplementary Fig. 1). Most of the reaction parameters are maintained across the different methods, with the exception of the choice of gold precursors. The nanowire synthesis using Au nanoparticles begins with transferring graphene to Quantifoil holey carbon TEM grids using a direct transfer method[36]. In brief, the Quantifoil TEM grid is placed onto a graphene-covered copper foil with the Quantifoil carbon film side facing the graphene. Then 2.5 μl of isopropyl alcohol (IPA) is dropped onto the sample to wet the interface, and the sample is dried at 85 °C on a hot plate for 15 min to promote adhesion between the Quantifoil carbon film and the graphene. The grid is floated on an

aqueous solution of 113 mM ammonium persulfate, $(NH_4)_2S_2O_8$, to etch the underlying copper foil and rinsed several times by floating the graphene transferred grid on deionized water. After the graphene transfer is complete, Au nanoparticles (either spherical nanoparticles or nanorods) dispersed in organic solvents are dropped and dried on the grids. Then, the grids are floated on an aqueous solution of 250 mM ammonium persulfate, $(NH_4)_2S_2O_8$, for 17 hours to initiate nanowire growth on the graphene and rinsed by transferring the grids to deionized water multiple times. In the nanowire synthesis process using a grid mesh as an Au precursor, a graphene-covered copper foil is partially cut before transferring the graphene to TEM grids, such that the Au grid mesh is exposed to the reaction solution during incubation. As a result, the density of the nanowires formed on graphene is higher near the exposed Au grid mesh.

Electron microscopy Conventional TEM images are captured using a JEOL JEM 2010F TEM operated at 200 kV and a JEOL JEM 2100 TEM operated at 200 kV. Low-resolution TEM and SEM images are captured using a Hitachi SU8000 FE-SEM operated at 30 kV.

Aberration-corrected TEM Aberration-corrected TEM images are captured with a TEAM 0.5 microscope at the National Center for Electron Microscopy at Lawrence Berkeley National Laboratory. The microscope is equipped with an image Cs aberration corrector and a monochromator. The images are acquired at 80 kV, and the Cs coefficient is set to approximately -10 μm. The TEM images are taken at an over-focus of 10 nm, which allows an optimal imaging condition with bright atom contrast.

AFM A Park Systems NX-10 AFM with an Olympus silicon microcantilever (AC160TS-C3, tip radius: 7 nm) is operated under ambient conditions.

Spectroscopy EDX point analysis is performed using a Noran Voyager III M3100 connected to a Hitachi HF-2000 FE-TEM (operation voltage: 100 kV). EDX elemental mapping is performed with a JEOL 2100F (operated at 200 kV), equipped with a field emission gun and a probe C_s corrector. EELS point spectra and EELS mapping at N K edge are acquired with a FEI Titan Cube G2 60-300 operated at 80 kV. Gatan GIF Quantum 965 is used as an EELS detector. Raman spectroscopy is performed using a Jasco NRS-5100 laser Raman spectrometer (excitation wavelength: 532 nm).

First-principles calculations The calculations for AuCN nanowires on graphene are performed using density functional theory (DFT) implemented in the Vienna Ab-initio Simulation Package (VASP) with a projector-augmented-wave (PAW) method. For the exchange correlation energy functional, the local density approximation (LDA) is employed, and the kinetic energy cutoff is taken to be 400 eV. The AuCN nanowire is obtained through minimization of the total energy, starting with (100) AuCN with a width of 1.7 nm and a height of 1.3 nm. In the initial structure for investigating the interaction between the nanowire and graphene, the AuCN nanowire is placed on single-layer graphene at a distance of ~3 Å. Geometry optimization of the structures is carried out until the Hellmann–Feynman force acting on each atom is smaller than 0.01 eV/Å. The plan-view of the unit cell is illustrated in Fig. 3a. The first Brillouin zone integration is performed using the Monkhorst–Pack scheme, and 10×4×1 k-point sampling for the nanowire is used. The binding energy between the nanowire and graphene is calculated by subtracting energies of the isolated nanowire and graphene from the total energy of the nanowire-graphene complex.

TEM image simulation from the crystal structure The TEM image simulations are performed using MacTempas and CrystalKit. The imaging acquisition conditions including a defocus value of 12 nm are used for the simulations of the AuCN crystal of 2 nm in thickness in the imaging crystal axis.

Graphene nanoribbon fabrication Graphene decorated with the nanowires is prepared on a TEM grid as described above. The graphene sample is then placed on a silicon wafer through the following method. First, a silicon wafer with thermal oxide is cleaned using oxygen plasma. The TEM grid is placed onto the wafer with the graphene side facing up. Then, 2.5 µL of IPA is dropped onto the sample to wet the interface between the backside of graphene and the silicon substrate. While the sample is dried at 85 °C on a hot plate for 1 hour, capillary forces generated by the evaporation of IPA promotes adhesion between the backside of the graphene and the silicon substrate. This process prepares the graphene to be sandwiched between the wafer and nanowires. The dry etching of graphene is performed using a Samco RIE-10 NR system with an oxygen gas flow rate of 10 sccm and a power of 30 W for 6.5 sec. Finally, the nanowires are etched off with a 0.42 M NaOH solution for 1 hour without damaging the graphene nanoribbons (Supplementary Fig. 10).

Supplementary Video legend

Supplementary Video 1. In-situ TEM video showing the nanowire decomposition to Au nanoparticle chains under e-beam irradiation with a 200 kV acceleration voltage and 106 µA beam current. The video (total area: 90.3 nm by 90.3 nm) has been accelerated by a factor of 50, displaying 5 fps (frames per second) while real time corresponds to 0.1 fps.

References in Supplementary Information

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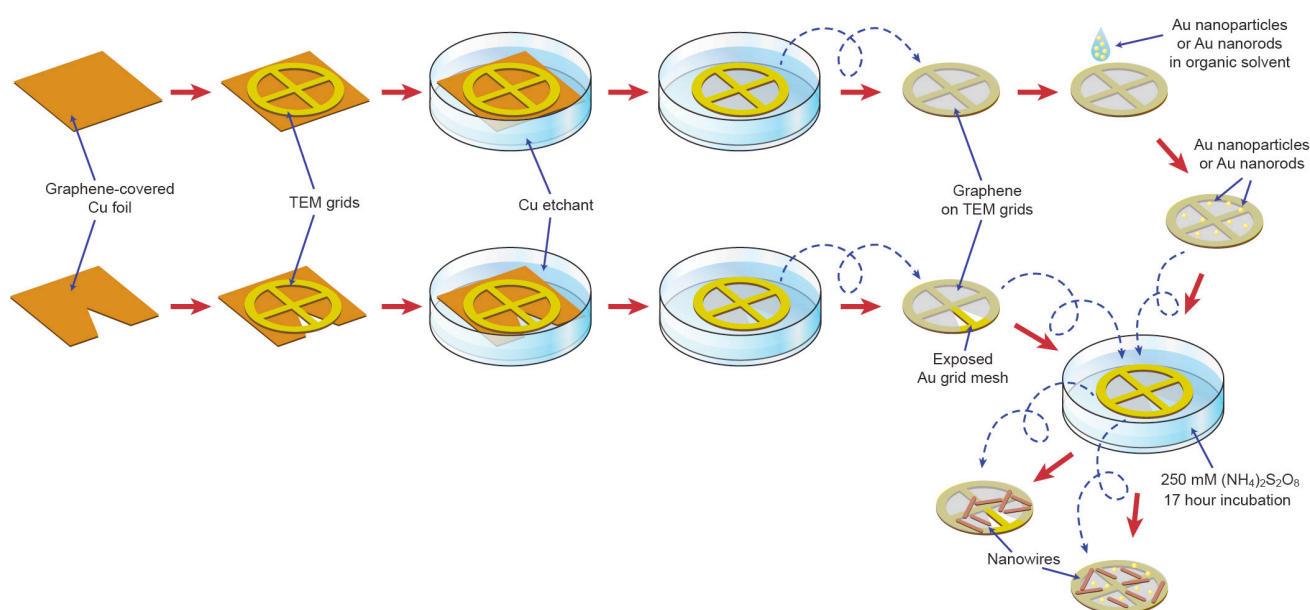
Supplementary Figure 1. Graphene transfer and nanowire synthesis. Three types of gold precursors are used for the nanowire synthesis in this study, with the majority of the remaining reaction parameters maintained constant. The nanowire synthesis using Au nanoparticles/nanorods (upper part in this figure) begins with transferring CVD-synthesized graphene to TEM grids. Then, Au nanoparticles/nanorods dispersed in organic solvents are dropped on the grids and dried. The nanowires are synthesized on graphene by floating the grids on an aqueous solution of 250 mM ammonium persulfate, $(NH_4)_2S_2O_8$, for 17 hours. In the nanowire synthesis using a grid mesh as an Au source (lower part in this figure), a graphene-covered copper foil is partially cut before the graphene is transferred to TEM grids. Then, without dropping the nanoparticles/nanorods, the grid is floated on the reaction solution for the nanowire synthesis. The Au grid mesh is partially exposed to the reaction solution during the incubation.
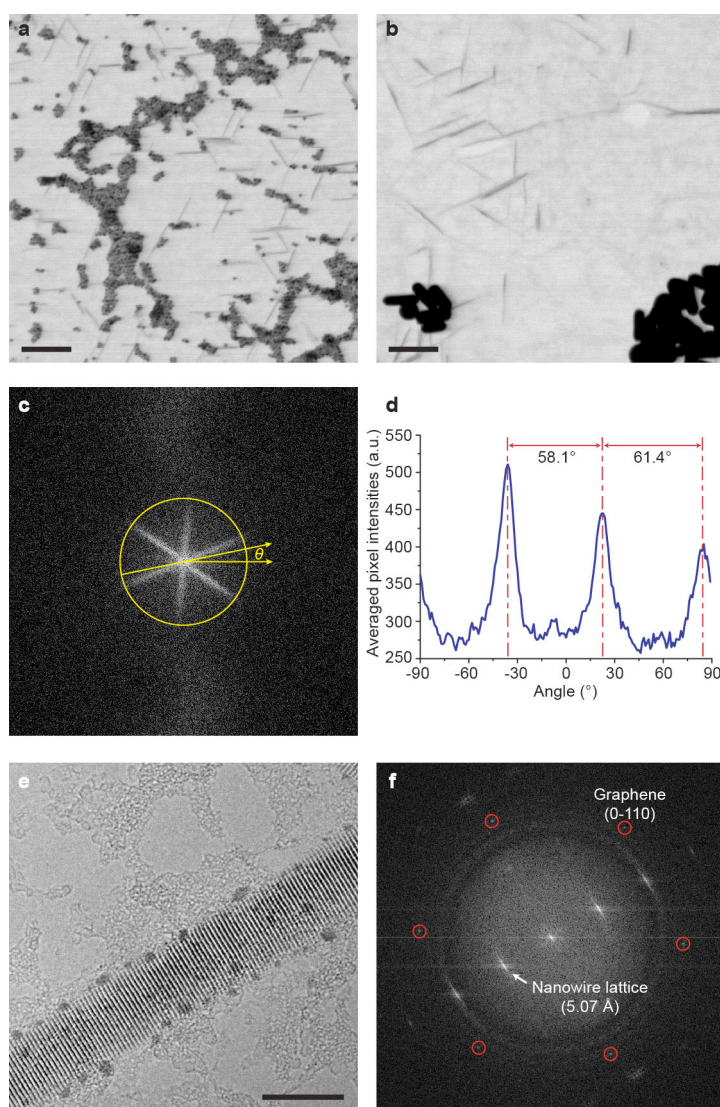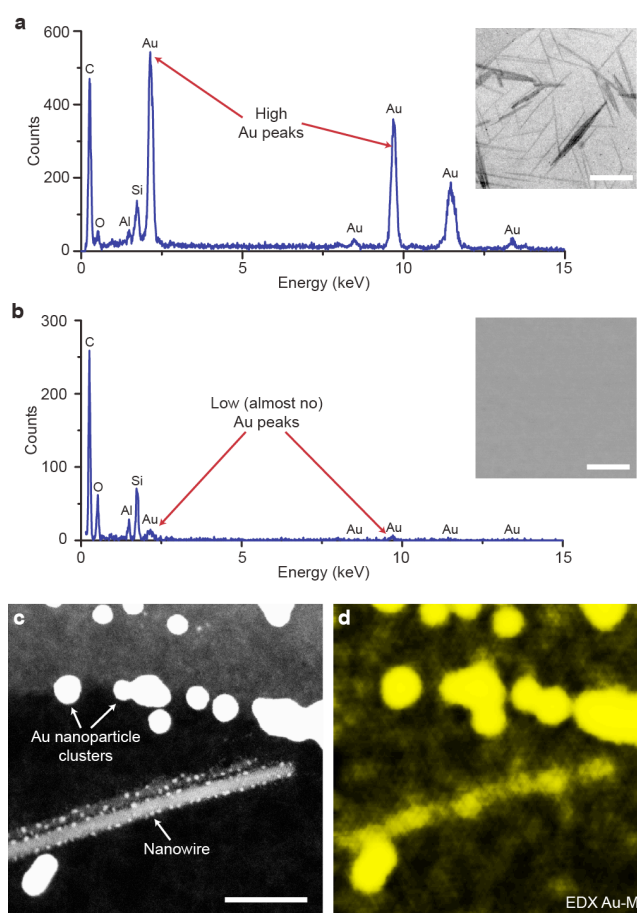
Supplementary Figure 2. TEM images of the nanowires. a–b, TEM images of the nanowires synthesized from various types of gold sources. Spherical Au nanoparticles (**a**), Au nanorods (**b**), or Au of TEM grids (Fig. 1b) are used in the nanowire synthesis. The scale bars represent 100 nm. **c**, Fourier transform of Fig. 1b. The directions of three bright lines are orthogonal to the directions of nanowire axes. **d**, Radial pixel intensities of **c** averaged along the line from the centre at different angles. The three peaks represent the nanowire alignment. **e**, High-resolution TEM image of a nanowire. The scale bar represents 10 nm. **f**, Fourier transform of **e**.
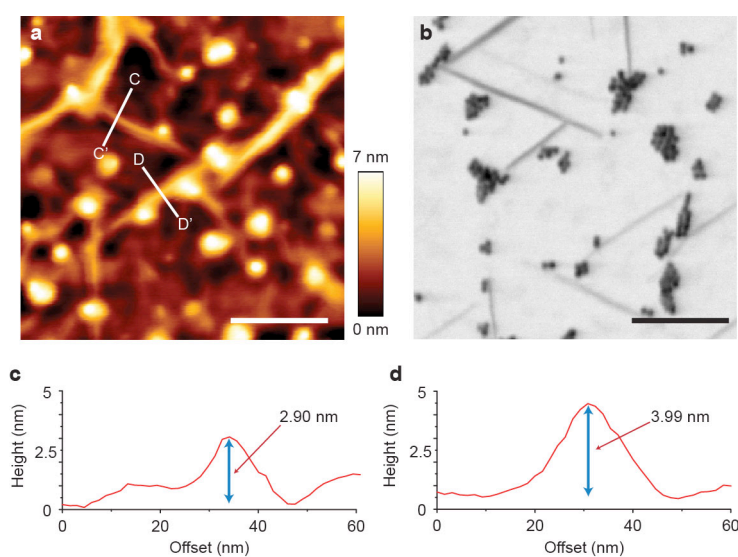
Supplementary Figure 3. AFM (Atomic force microscopy) analysis of the nanowires. a, AFM image of the nanowires synthesized from Au nanoparticles. The bright dots show Au nanoparticle clusters, and the bright lines are the synthesized nanowires. The scale bar represents 100 nm. **b**, TEM image of the same sample as **a**. The scale bar represents 100 nm. **c–d**, Height profiles of the sample along the C–C' (**c**) and D–D' (**d**) lines in **a**. The nanowire thickness is measured as 3.29 ± 0.47 nm from 7 repeated measurements.
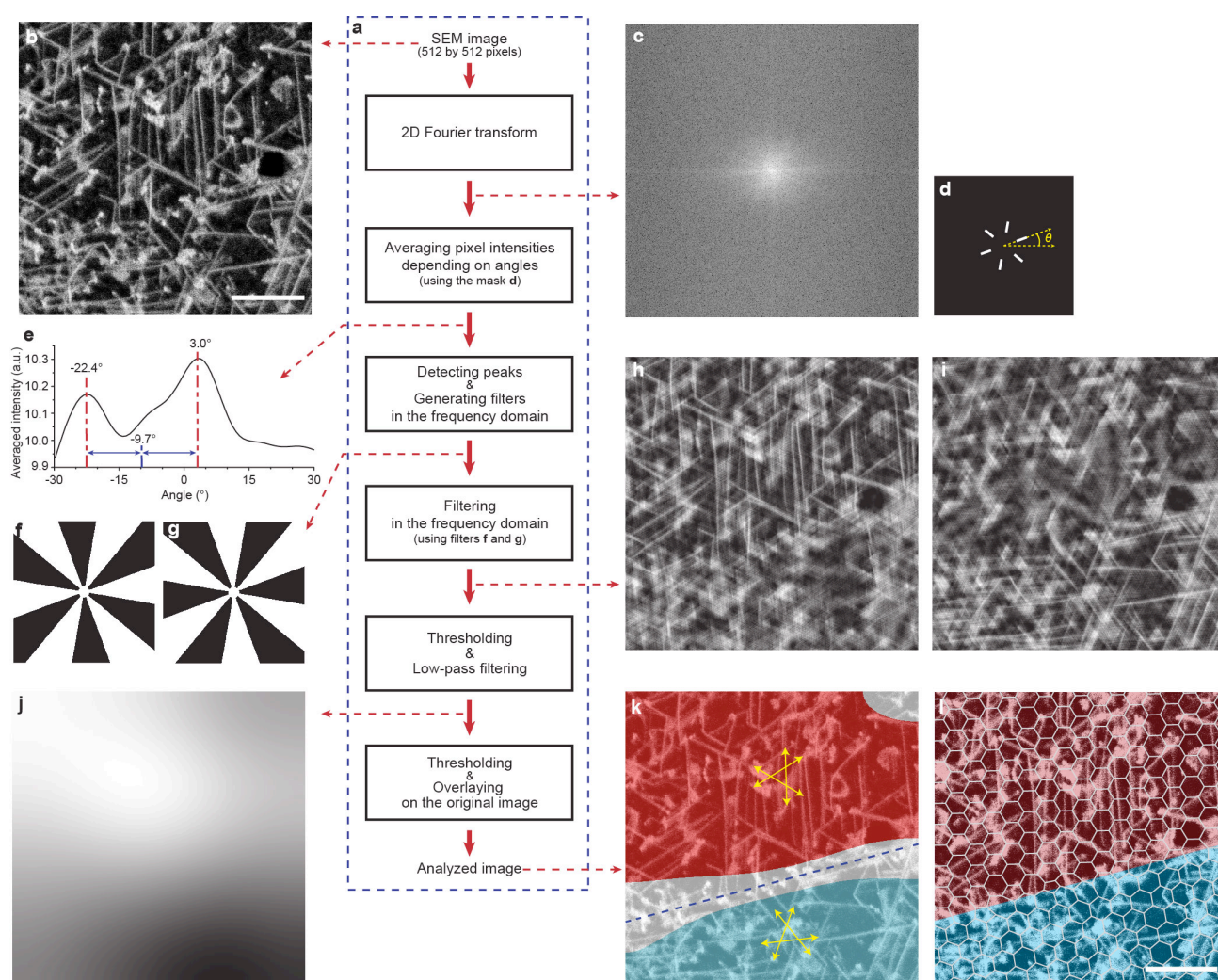
Supplementary Figure 4. Automated image processing for the SEM-based visualization of crystal directions and grain boundaries in polycrystalline graphene. a, Process chart for the automated image processing. **b**, Initial SEM image of the nanowires on polycrystalline graphene. The scale bar represents 100 nm. **c**, Fourier transform of **b**. **d**, Mask image for averaging the pixel intensities of **c**. **e**, Averaged pixel intensities of **c** depending on the angles, θ. The two peaks present two graphene grains whose crystal directions are tilted relative to each other. **f-g**, Frequency-domain filters for the image separation of the two graphene grains. **h-i**, Filtered images of **b** using **f** and **g**. The nanowires on the bottom part and the upper part of the original image (**b**) are selectively filtered out in **h** and **i**, respectively. **j**, Black and white map representing the difference in nanowire densities in **h** and **i**. **k-l**, Initial SEM image (**b**) with overlays of colour maps calculated from the automated image processing (**k**) and manually obtained (**l**). The red and blue colour maps represent different grains tilted relative to each other. The spatial resolution of the automated image processing is approximately 100 nm for this experimental condition.

Supplementary Figure 5. Energy-dispersive X-ray spectroscopic (EDX) analysis of the nanowires. a–b, EDX spectra of the nanowires on graphene (**a**) and graphene substrate without the nanowires (**b**). The spectra are measured from the entire areas of the insets. The scale bars indicate 100 nm. The peaks indicate the presence of Au within the nanowires. **c–d**, EDX chemical mapping of the sample. The ADF TEM image (**c**) and the gold chemical map (**d**) are displayed. The scale bar indicates 25 nm.
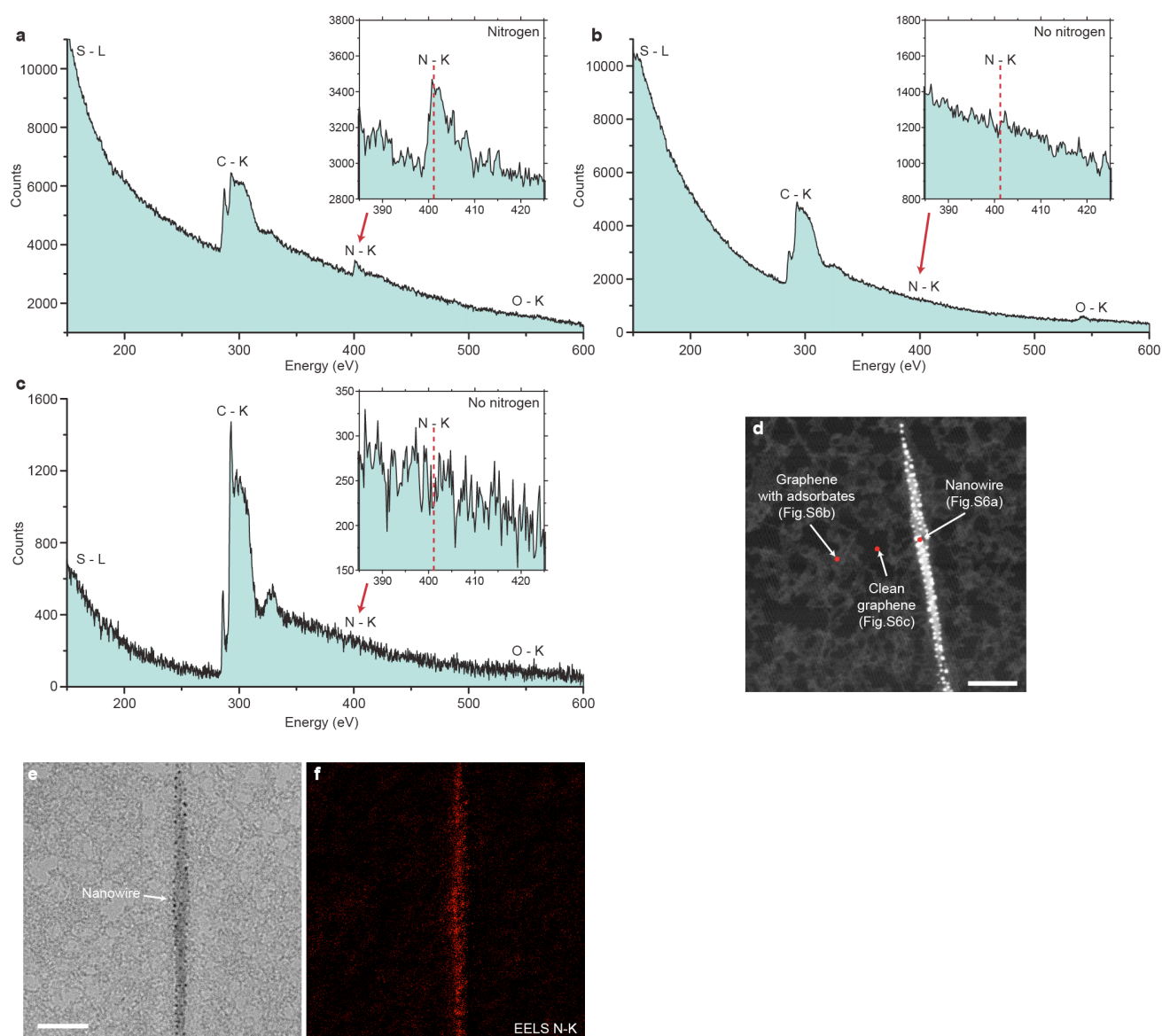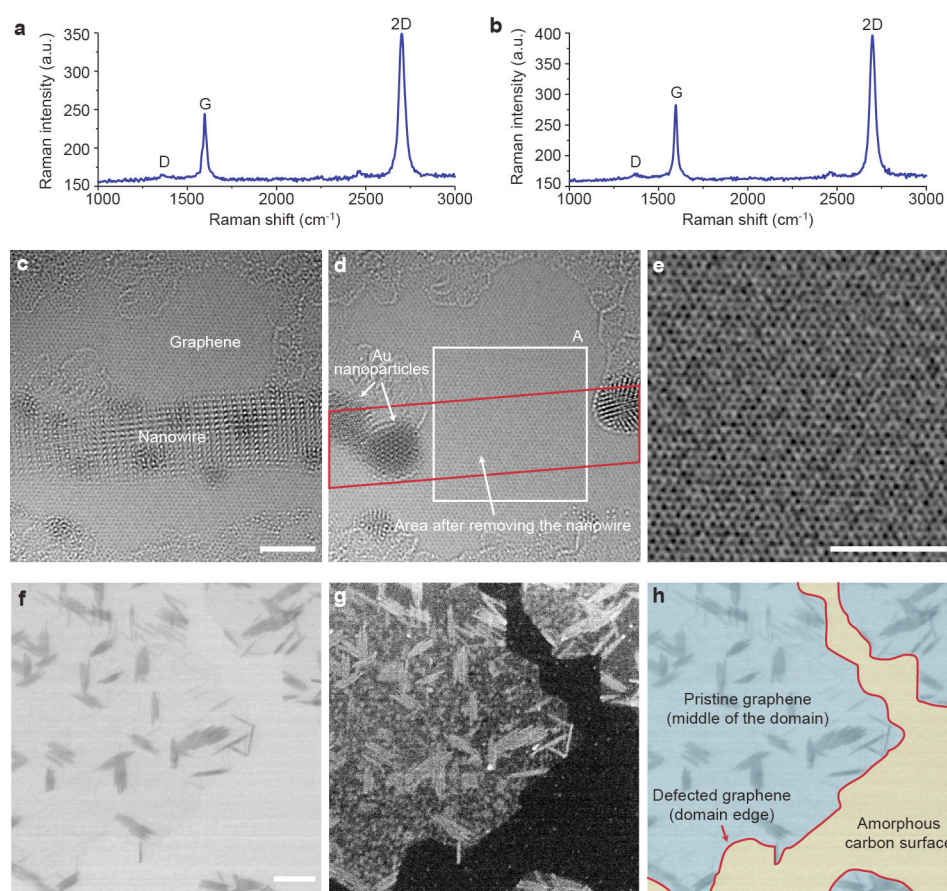
Supplementary Figure 6. Electron energy loss spectroscopic (EELS) analysis of the nanowires. a–c, EELS spectra of the nanowires on graphene (**a**), a graphene area with adsorbates (**b**), and a clean graphene area (**c**). The peaks indicate the presence of N within the nanowires. **d**, ADF TEM image showing three points for the EELS measurements in **a**, **b**, and **c**. Scale bar: 40 nm. **e–f**, EELS chemical mapping of the sample. The TEM image (**e**) and the energy-filtered TEM image at the N K-edge (**f**) are displayed. Scale bar: 25 nm.
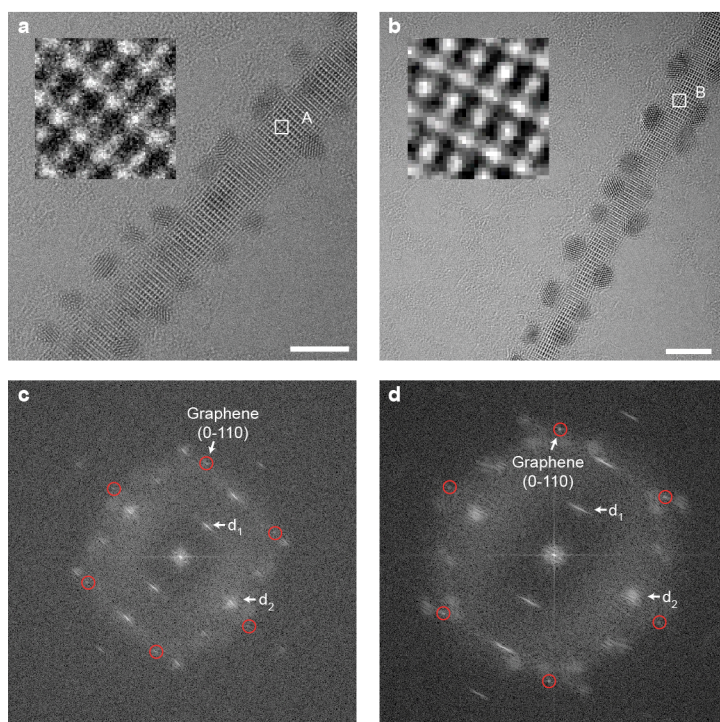
Supplementary Figure 7. Atomic-resolution TEM images of the nanowires. a–b, Atomic-resolution TEM images of the nanowires. The insets show enlarged views of the portions A and B, respectively. The inset in **a** is the same image as Fig. 2a. The scale bars indicate 5 nm. **c–d**, Fourier transforms of the TEM images. The first-order graphene diffraction spots are marked by red circles. The first-order diffraction spots from the nanowires are indicated by two arrows, d_1 and d_2. d_1 in **c**: 5.08 ± 0.01 Å, d_2 in **c**: 3.00 ± 0.12 Å, d_1 in **d**: 5.07 ± 0.01 Å, and d_2 in **d**: 3.00 ± 0.16 Å.
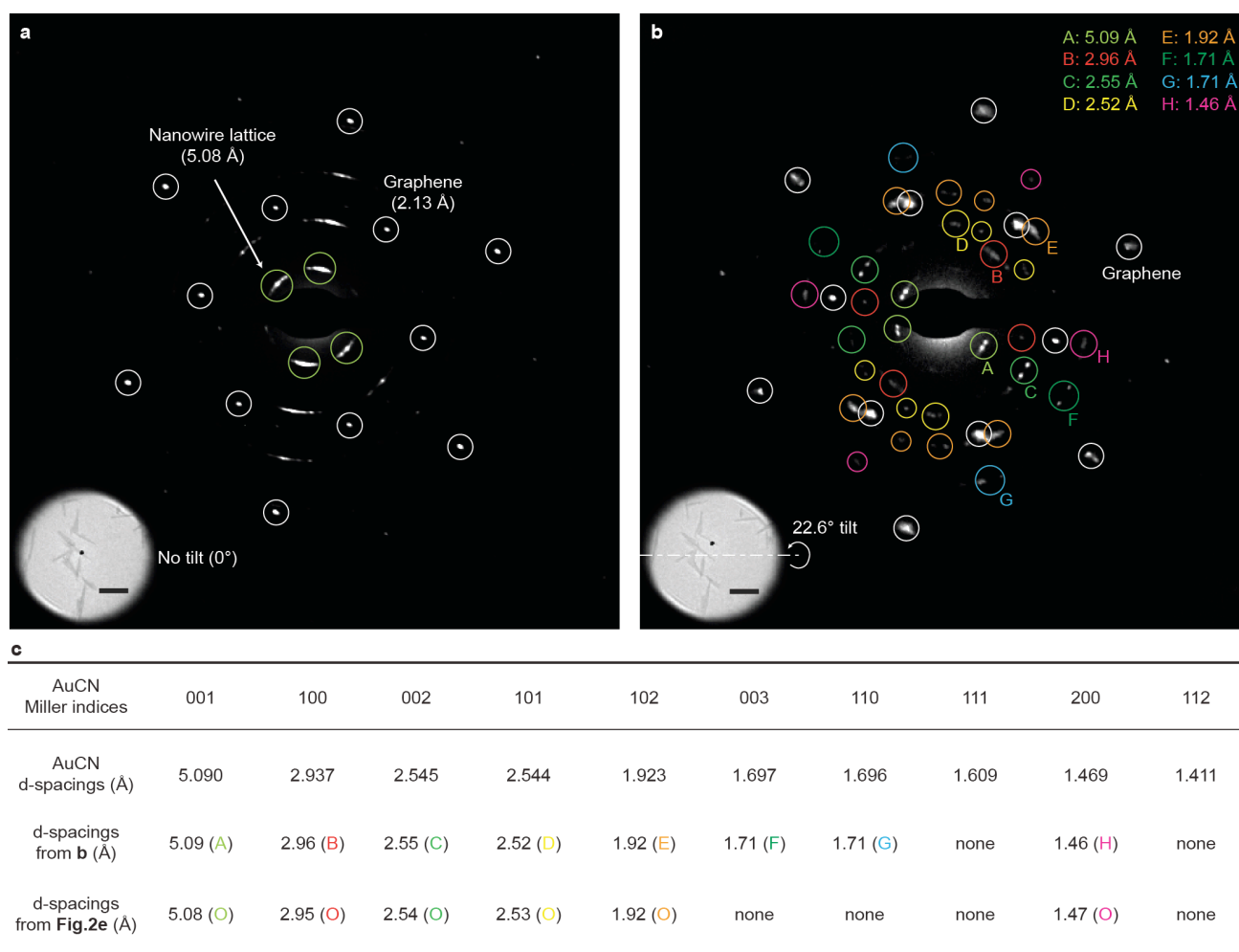
Supplementary Figure 8. Comparison of d-spacings of an AuCN crystal and the nanowires. a–b, SAED patterns of a nanowire-graphene sample under no tilt (a) and a 22.6° tilt (b). The insets show the sample areas where the SAED patterns are measured. Scale bar: 100 nm. c, D-spacings obtained from an AuCN crystal and measured from SAED patterns of tilted nanowire samples. The matched d-spacings confirm that the synthesized nanowire is AuCN.

AuCN Miller indices	001	100	002	101	102	003	110	111	200	112
AuCN d-spacings (Å)	5.090	2.937	2.545	2.544	1.923	1.697	1.696	1.609	1.469	1.411
d-spacings from b (Å)	5.09 (A)	2.96 (B)	2.55 (C)	2.52 (D)	1.92 (E)	1.71 (F)	1.71 (G)	none	1.46 (H)	none
d-spacings from Fig.2e (Å)	5.08 (O)	2.95 (O)	2.54 (O)	2.53 (O)	1.92 (O)	none	none	none	1.47 (O)	none

Supplementary Figure 9. Verification of the pristine state of graphene on which the nanowires are synthesized. a–b, Raman spectra of graphene before (**a**) and after (**b**) the nanowire growth. **c–e**, Atomic-resolution TEM images of a nanowire on graphene before (**c**) and after (**d**, **e**) removing the nanowire. The nanowire on graphene in the initial sample (**c**) is decomposed by e-beam irradiation (Fig. 4) in order to image the graphene surface underneath the nanowire (**d**). The enlarged and low-pass filtered image (**e**) of the section A in **d** confirms the pristine state of the graphene underneath the nanowire. The scale bars indicate 3 nm. **f–g**, Concurrently captured TEM (**f**) and SEM (**g**) images of the nanowires synthesized on graphene pieces transferred onto amorphous carbon films. The TEM (**f**) and SEM (**g**) images clearly show synthesized nanowires and graphene-covered areas, respectively. The scale bar indicates 100 nm. **h**, Coloured TEM image which differentiates graphene-covered areas from amorphous carbon films.
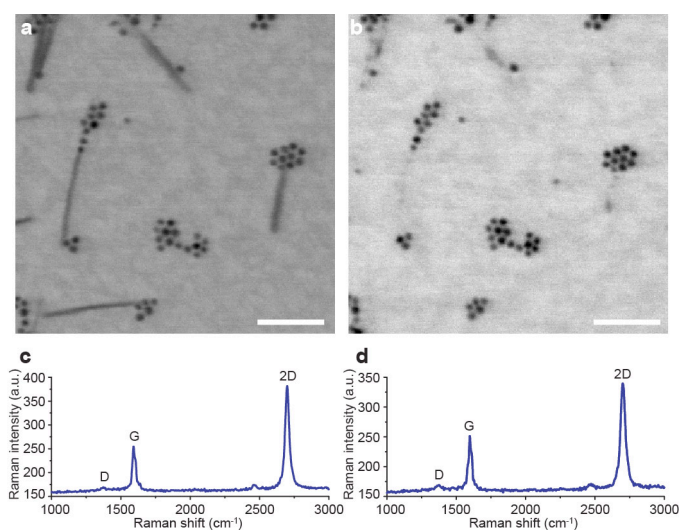
Supplementary Figure 10. Nanowire etching. a–b, TEM images of the sample before (**a**) and after (**b**) the nanowire etching process. The scale bar indicates 50 nm. **c–d**, Raman spectra of the sample before (**c**) and after (**d**) the nanowire etching process.
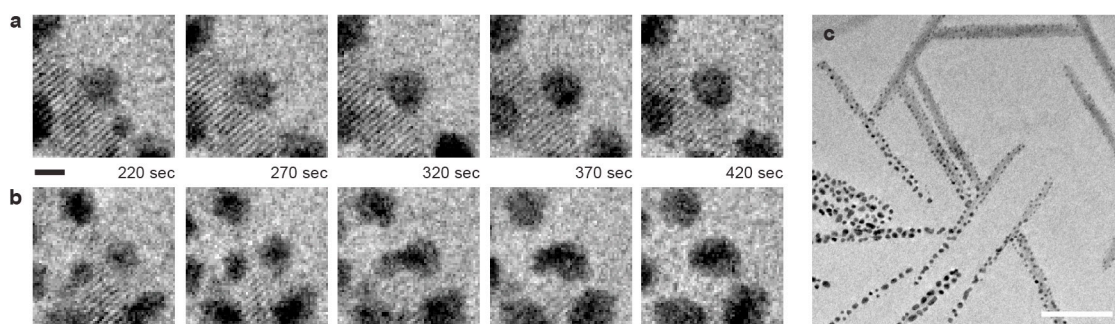
Supplementary Figure 11. Nanowire decomposition to Au nanoparticles under e-beam irradiation. a–b, A series of TEM images from Supplementary Video 1 for two different growth trajectories of Au nanoparticles: monomer addition (**a**) and coalescence (**b**). The scale bar indicates 2.5 nm. **c**, Au nanoparticle chains formed in the selected area (bottom-left corner) by irradiating the e-beam at the bottom-left corner. The scale bar indicates 50 nm.