

Supporting Information for ...Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated  
Atom Transfer Radical Polymerization ... by Michael C. P. Wang, and Byron D. Gates\*

## Supporting Information for ...

### *Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated Atom Transfer Radical Polymerization*

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## Experimental

Anisotropic nanostructures of single crystalline *t*-Se were synthesized by a hydrothermal process without the assistance of surfactants, which are commonly used to facilitate the formation of anisotropic nanostructures.<sup>1-2</sup> Surfactants are used in other syntheses to prevent the nanostructures from aggregating, and serve as protective barriers between nanostructures' surfaces and the surrounding chemical environment. The absence of surfactants or other coatings on the surfaces of the selenium nanostructures expose its surfaces to oxidative damage by oxygen and moisture.

**Synthesis of 1D *t*-Se nanostructures:**<sup>3</sup> One dimensional selenium nanostructures were synthesized from amorphous selenium colloids. The selenium colloids were synthesized by reducing selenious acid with hydrazine. For example, 2.73 g (21.1 mmol) of selenious acid (H<sub>2</sub>SeO<sub>3</sub>; 98%; Sigma-Aldrich) was dissolved in 100 mL of 18 MΩ•cm water (purified with Barnstead Nanopure DIamond Life Science water filtration system) with magnetic stirring in a 250 mL round bottom flask. The solution was cooled to ice-water temperatures before slowly adding 3 mL (61.1 mmol) of ice cooled reducing agent, hydrazine (N<sub>2</sub>H<sub>4</sub>; 50-60%; Sigma-Aldrich). Hydrazine was introduced in a drop-by-drop manner into the reaction solution under magnetic stirring over a period of 2 min. The reaction was allowed to proceed for another 15 min while at ice-water temperatures before the brick red precipitate was collected by vacuum filtration onto a PVDF filter membrane with an average pore size of 0.1 μm (catalogue number VVLP04700; Millipore). The filtrate was rinsed with 200 mL of deionized water to remove residual hydrazine. The filtered precipitate of selenium colloids was stored in a plastic petri-dish wrapped in aluminum foil and freeze dried in a Savant Modulyo lyphoilizer (Thermo Scientific) at -50 °C and 100 mbar for 12 h.

Anisotropic *t*-Se were synthesized from amorphous selenium colloids by a

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solvochemical method. Selenium colloids (1 mg) were combined with ethanol (EtOH; 2 mL; 95%; Commercial Alcohols) in a 2 dram glass vial. Then the colloids were dispersed in the EtOH by immersion for 20 s in a sonication bath (Branson Model 1510). The solution was then placed in a dark cabinet maintained at 22 °C to allow the reaction to reach completion over a period of ~12 h. The resulting nanostructures are single crystalline as characterized by selected area electron diffraction.<sup>4</sup>

**Synthesis of *t*-Se@PS nanostructures:** Selenium nanostructures dispersed in EtOH (2 mL; 233 mg/mL) were separated from their dispersant via centrifugation (13,500 rpm for 15 min). The solvent was decanted and replaced with dichloromethane (DCM; 99%; Caledon) to re-disperse the selenium nanostructures. This process was repeated twice in total to remove residual ethanol. Finally, selenium was re-dispersed in 10 mL of DCM, which was combined with 10 mL of styrene (99%; Sigma), and 10 mL of hexanes (>98.5%; EMD Millipore) in a three-necked round bottom UV reactor. Nitrogen was bubbled via a glass pipette through the reaction mixture for 10 min while cooling the solution to ice-water temperatures. Then the glass pipette was elevated above the reactants to maintain the inert atmosphere over the next 6 h of UV irradiation. The UV light source was a mercury pencil lamp (Oriol Instruments Model 6035; see **Fig. S7** for emission spectrum) powered by a DC power supply (Oriol Instruments Model 6060). Final product, *t*-Se@PS, was purified by centrifugation (13,500 rpm for 15 min) and rinsed with a solution of 1:1 hexanes to EtOH (v:v) after decanting the original solvent. The product was purified three times in total, before it was redispersed in EtOH.

As a control experiment, ~10-50 nm PS colloids were first synthesized by UV initiated polymerization of styrene in the absence of *t*-Se while under constant magnetic stirring, nitrogen purged conditions, and at ice-water temperature. Throughout 6 h of UV irradiation, the reaction mixture was kept under nitrogen

Supporting Information for ...Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated Atom Transfer Radical Polymerization ... by Michael C. P. Wang, and Byron D. Gates\*

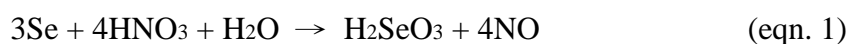
atmosphere and at ice-water temperatures. Then *t*-Se was introduced into the reaction flask and the reaction mixture was left a room temperature (RT) for 15 h before it was purified by the method described in the paragraph above. Bright field TEM images revealed that there are micrometer and nanometer sized PS colloids (**Fig. S5a**) mixed together with *t*-Se@PS nano-composites (**Fig. S5b**). Some of the nano-composites have large PS colloids attached to their surfaces (**Fig. S5c**).

**Materials Characterization Techniques:** Transmission electron microscopy (TEM) images, energy-dispersive X-ray spectroscopy (EDS) and selected area electron diffraction (SAED) data were obtained with either an FEI Tecnai G<sup>2</sup> F20 scanning TEM (STEM) with a field emission gun thermionic source operating at 200 kV, or a Hitachi 8000 STEM with a lanthanum hexaboride thermionic source operating at 200 kV. For TEM analysis, samples were prepared by drop-casting or dip-coating solutions of nanostructures onto a 300 mesh copper grid coated with formvar/carbon (catalogue number: FCF300\_CU\_50; Cedarlane Laboratories Ltd.). To test the resistance of the *t*-Se@PS nanostructures to oxidation and corrosion, these samples were immersed into 1% and 30% aqueous solution of hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>; Caledon) before they were drop-casted onto TEM grids. Selenium samples without surface passivation by PS were prepared by dipping a TEM grid containing *t*-Se nanostructures into 1% H<sub>2</sub>O<sub>2</sub> for 5 s before it was flash frozen on a block of aluminum that had been cooled to liquid nitrogen temperatures. The frozen solution was removed by lyophilization before TEM analysis.

To test the *t*-Se@PS composite's ability at resisting corrosion against ionic etchant, such as nitric acid (68-70% HNO<sub>3</sub>; Anachemia). First, the composite material dispersed in EtOH was collected via centrifugation (8,500 rpm for 15 min). The material was rinsed with 1 mL of DI water for a total of 3 times to remove residual

Supporting Information for ...Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated Atom Transfer Radical Polymerization ... by Michael C. P. Wang, and Byron D. Gates\*

EtOH. Then 1 mL of 30% of HNO<sub>3</sub> was added into the centrifuge tube containing the *t*-Se@PS nano-composite material. The nano-composites were immersed in the ionic etchant at RT for 1 h before decanting the solution. The products were rinsed with 1 mL of DI water 3 times to remove residual acid before redispersing the nanostructures in 1:1 EtOH to hexanes (v:v) for TEM sample preparation. As a control, concentrated HNO<sub>3</sub> was added to a sample of *t*-Se after removal of the EtOH under vacuum. Concentrated HNO<sub>3</sub> dissolved the *t*-Se in ~10 min (eqn. 1; see **Fig. S8**).<sup>5</sup>



X-ray photoelectron spectroscopy (XPS) analysis was carried out on a Kratos Analytical Axis Ultra DLD spectrometer using a monochromatic aluminum source (AlK $\alpha$ , 1486.6 eV) operating at 150 W (10 mA emission current and 15 kV HT). Analysis was conducted on a 700 x 300  $\mu\text{m}^2$  area of the sample. High resolution scans were obtained at a 25 meV step size with a dwell time of 1000 ms per step, a pass energy of 20 eV, and averaged over 4 scans. Energy scale linearity was calibrated using Al and Mg X-ray sources on Argon sputter cleaned gold and copper substrates. The calibration procedure was performed in accordance to ISO 15472 international procedure. XPS samples were prepared by drop-casting dispersions of *t*-Se and *t*-Se@PS onto a ~1x1 cm<sup>2</sup> SiO<sub>x</sub>/Si substrate. The as-synthesized *t*-Se sample (**Fig. S1a**) cast on SiO<sub>x</sub>/Si was left at ambient conditions (RT, and ~1 atmosphere) in a plastic petri-dish (VWR; catalogue number: 89038-968) for a month before XPS analysis for oxidation of the *t*-Se nanostructures (**Fig. S1b**). Selenium oxide was removed by immersing the *t*-Se nanostructures deposited on a SiO<sub>x</sub>/Si substrate in a bath of 1% hydrofluoric acid (diluted from 48% non-buffered HF, EMD Millipore) for 2 min (**Fig. S1c**).

Secondary ion mass spectrometry (SIMS) was carried out on a Hiden Analytical

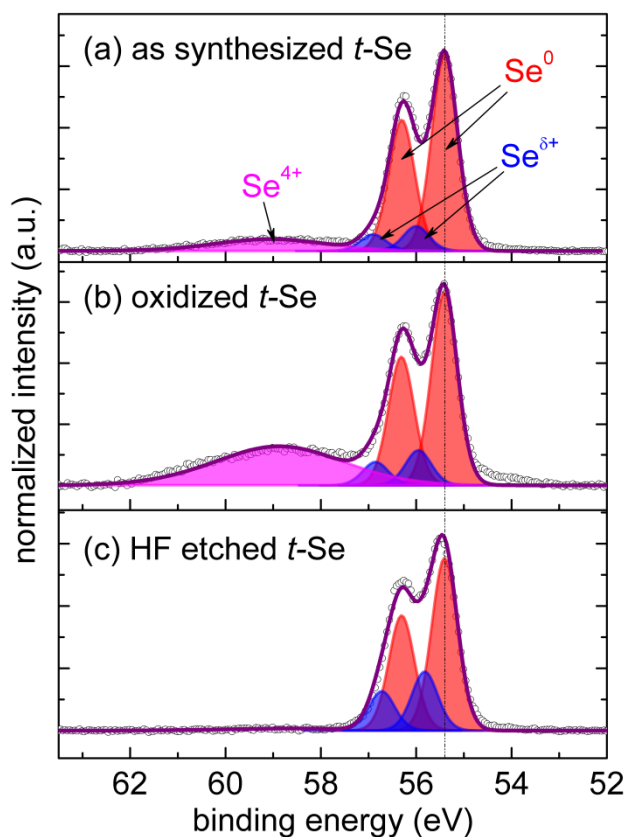
Supporting Information for ...Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated  
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Ltd. instrument fitted with an IG20 gas ion gun and a triple quadrupole MAXIM mass spectrometer. Samples were sputtered with 5 keV Argon ions that were used to produce positive and negative ions species. SIMS samples were prepared by drop-casting dispersions of *t*-Se and *t*-Se@PS onto a  $\sim 1 \times 1 \text{ cm}^2$  Au (100 nm thick) coated Si substrate.

Photoemission spectrum of the mercury pen lamp was recorded on a PTI Quantamaster spectrofluorometer.

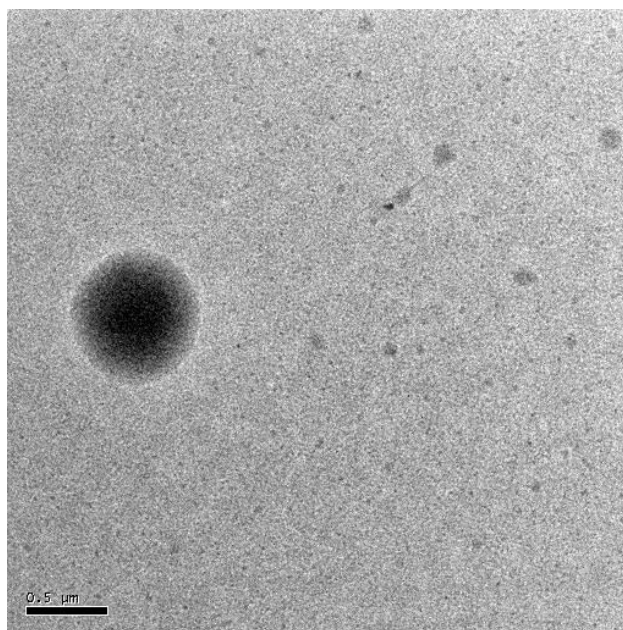
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## Figures

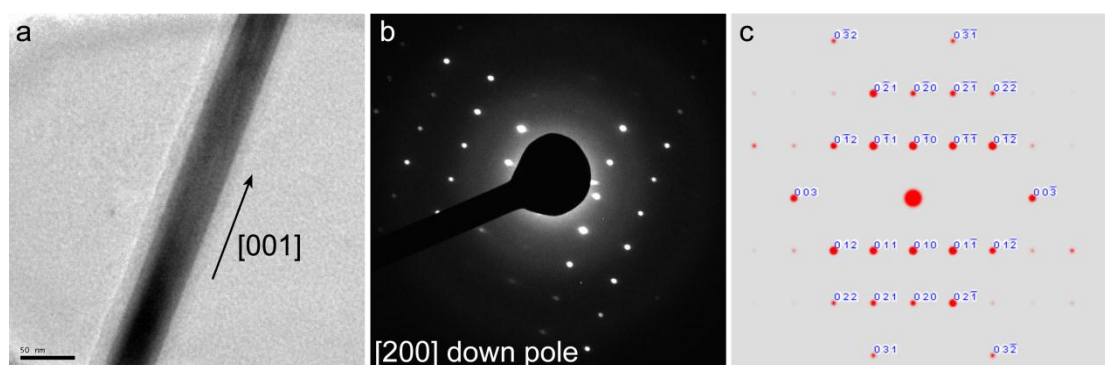


**Fig. S1** High resolution Se3d photoelectron emission spectra of (a) as-synthesized *t*-Se, (b) oxidized *t*-Se, and (c) HF etched *t*-Se are deconvoluted. The doublet colored in red is the emission peaks (Se3d<sub>3/2</sub> and Se3d<sub>5/2</sub>) from elemental selenium (Se<sup>0</sup>). The doublet colored in blue has a higher binding energy in comparison to that of elemental selenium indicates that these species of selenium (Se<sup>δ+</sup>) atoms exist next to an electron withdrawing neighbor, such as water molecules (see Supporting Information **Fig. S6**). The broad singlet at ~59 eV is a signature of Se<sup>4+</sup> species,<sup>6</sup> which can be etched away with water, hydrofluoric acid, and other non-oxidative acids. The as-synthesized *t*-Se sample was stored at ambient conditions (e.g., atmospheric pressure, room temperature, and away from light in a drawer) for one month. After this period of time, a noticeable change was observed in the amount of selenium dioxide (SeO<sub>2</sub>; Se<sup>4+</sup>) present. The oxide was removed by a brief immersion in HF acid (see Experimental section for further details).

Supporting Information for ...Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated  
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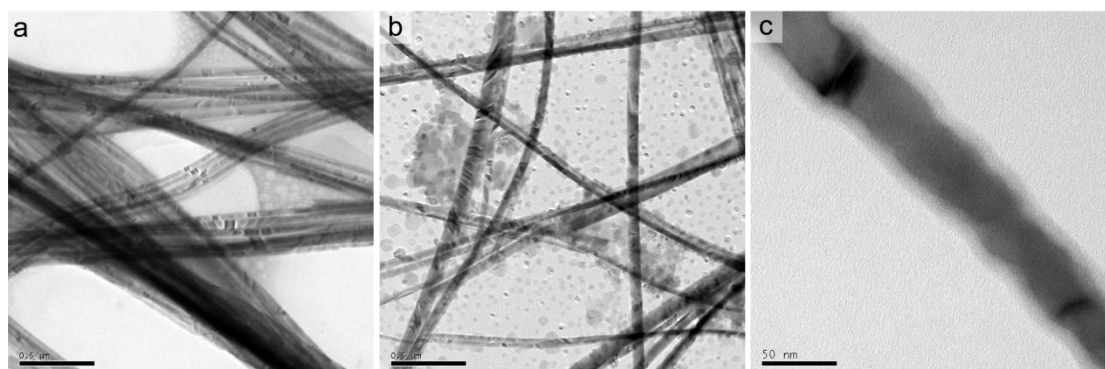
**Fig. S2** TEM analysis indicated that polydispersed polystyrene colloids were produced from the UV initiated radical polymerization in the absence of one dimensional *t*-Se nanostructures. Scale bar is 500 nm.



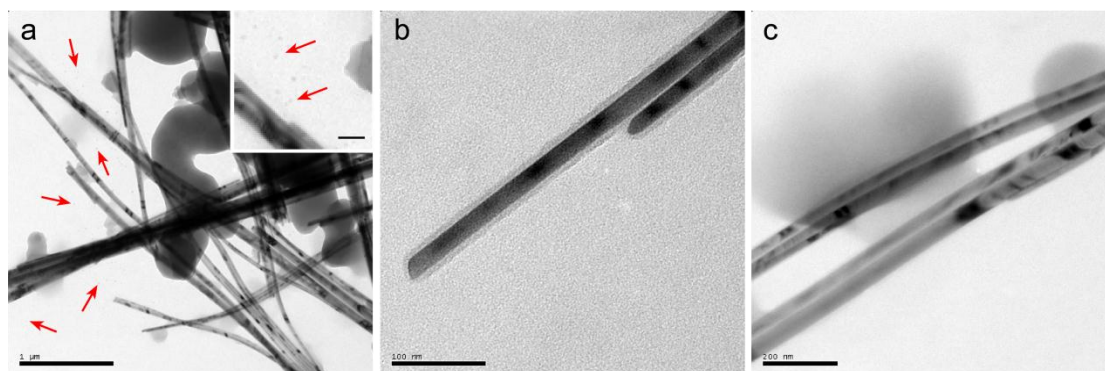
**Fig. S3** Bright field TEM microscopy image (a) of a single strand of *t*-Se@PS nanostructure and its corresponding (b) electron diffraction images that indicates *t*-Se remained single crystalline after the radical initiated reaction. The acquired electron diffraction pattern is a match to a (c) simulated single crystal diffraction pattern of *t*-Se in [200] down pole produced by CrystalMaker<sup>®</sup>. Scale bar is 50 nm.



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Atom Transfer Radical Polymerization ... by Michael C. P. Wang, and Byron D. Gates\*

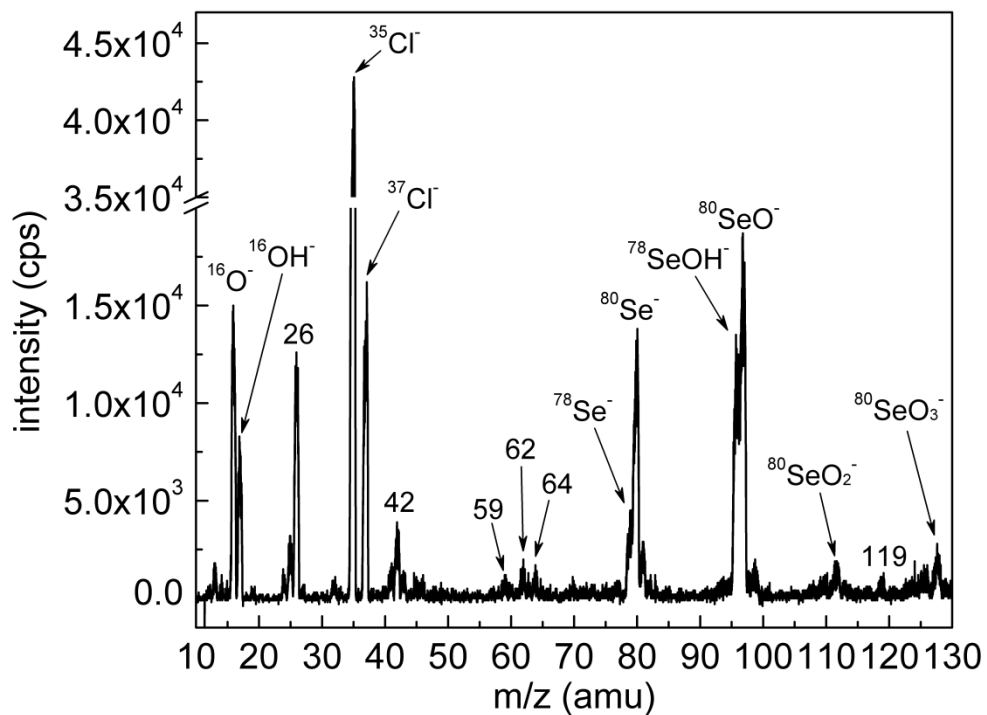


**Fig. S4** Performing radical initiated polymerization without controlling the reaction temperature can produce undesired by-products such as a) polystyrene coating that encapsulated multiple *t*-Se nanostructures, b) polystyrene colloids, and c) heat induced degradation of the *t*-Se nanostructures. Scale bars in (a) and (b) are 500 nm; and 50 nm in (c).



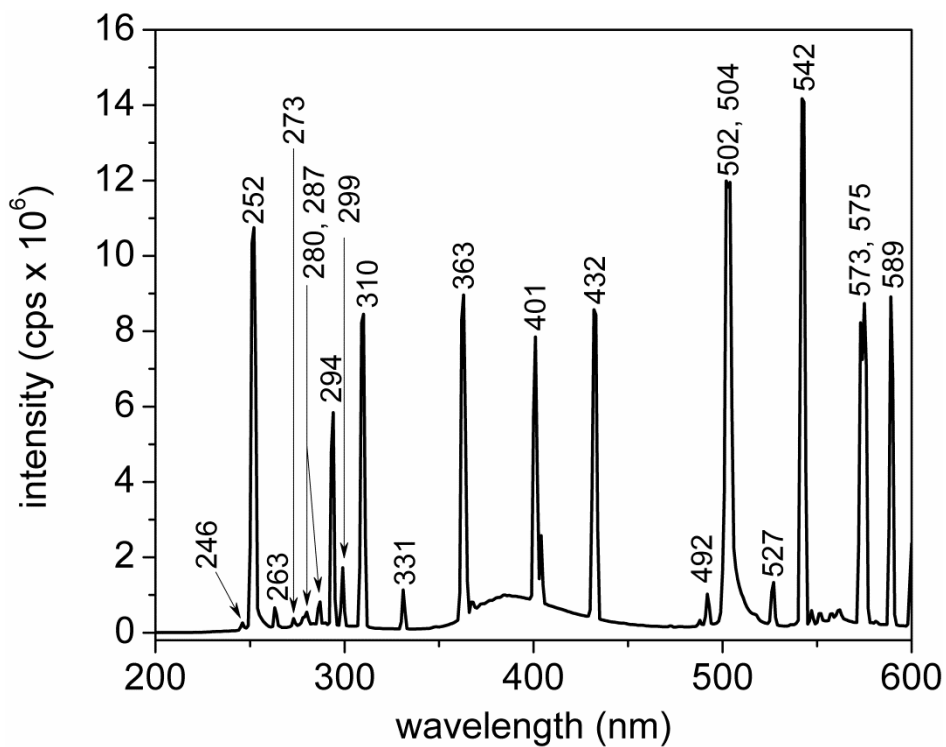
**Fig. S5** Bright field TEM images demonstrated that the control reaction of exposing the styrene to UV for 6 h and then combining this solution with *t*-Se nanostructures produced (a) micrometer and nanometer (red arrows and inset) sized PS colloids along with (b) *t*-Se@PS nano-composites. Some of the (c) nano-composites have large PS colloids attached to their surfaces. Scale bars are (a) 1  $\mu$ m (100 nm for the inset), (b) 100 nm; and (c) 200 nm.

Supporting Information for ...Synthesis of Selenium Nano-Composite (*t*-Se@PS) by Surface Initiated  
Atom Transfer Radical Polymerization ... by Michael C. P. Wang, and Byron D. Gates\*

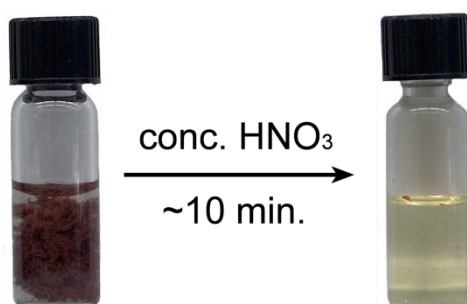


**Fig. S6** Presence of water, which fragmented into OH<sup>-</sup>, and fragments of selenium dioxide (SeO<sup>-</sup>, SeO<sub>2</sub><sup>-</sup>, and SeO<sub>3</sub><sup>-</sup>) are detected by secondary ion mass spectrometry (SIMS) on the surfaces of anisotropic *t*-Se nanostructure.

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Atom Transfer Radical Polymerization ... by Michael C. P. Wang, and Byron D. Gates\*



**Fig. S7** A spectrofluorometer was used to acquire the photoemission spectrum of the mercury pen lamp used to initiate the polymerization of styrene on the surfaces of selenium nanostructures.



**Fig. S8** Anisotropic trigonal selenium nanostructures dissolved in concentrated nitric acid (70% HNO<sub>3</sub>) producing a transparent solution of selenious acid and nitric oxide.<sup>5</sup>

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