

Supporting Information

Distinct reactivities on segmented selenium nanorods

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Experimental Section

Chemicals. Carboxymethyl-cellulose (CMC, Sodium salt, Low viscosity), selenium dioxide (SeO_2 , 98%), (3-mercaptopropyl)trimethoxy-silane (MPTMS, 95%), hydrogen tetrachloroaurate(III) trihydrate (HAuCl_4) and sodium silicate solution (Na_2SiO_3 , ca. 27% in 14% $\text{NaOH}_{(\text{aq})}$) were purchased from Sigma-Aldrich. Sodium borohydride (NaBH_4 , powder) were purchased from Riedel-deHaën. Hydrazine anhydrous solution (N_2H_4 , 1 M in THF) was purchased from Fluka. All chemicals were used without further purification.

Preparation of Symmetry-Breaking Segmented Selenium Nanorods (SBS-SeNRs). Selenium nanorods were prepared according to our established method.¹ In a typical synthesis of SBS-SeNRs around 700 nm in length, briefly, 0.082 g of SeO_2 powder was completely dissolved in 10 mL of 3.9 wt% CMC solution under moderate stirring. Subsequently, 1 mL of 0.74 mM freshly prepared NaBH_4 solution was added dropwise into the above solution for 4 min of reaction. Afterwards, the solution was placed into 70 °C oven without any agitation for 1 h. The collected product was directly dispersed into deionized water for further surface modification.

Preparation of Silica-Coated SBS-SeNRs Core/shell nanostructures were demonstrated in the two forms of solid and hollow type SBS-SeNR@ SiO_2 nanofloats. For synthesizing solid type SBS-SeNR@ SiO_2 nanofloats, 100 μL of SBS-SeNRs solution was added into a 50 mL plastic bottle containing 25 mL of deionized water

with magnetic stirring. Afterwards, 1 mL of 0.05 mM MPTMS/EtOH solution was added dropwise into the above solution under standard stirring. The reaction was allowed to proceed for 30 min, followed by washing with deionized water by centrifugation. The collected particles displayed in the form of solid type SBS-SeNR@SiO₂ nanofloats. For the hollow type, another 200 μL of 0.05 wt% sodium silicate solution was introduced into the reaction solution while the MPTMS modification was formed. The solution was allowed to proceed for another 30 min. The resulting nanoparticles were purified and washed with ethanol by centrifugation in order to extract the un-condensed organo-silane molecules, and thus forming hollow type SBS-SeNR@SiO₂ nanofloats.

Selective Reactivities on *t*-Se Segment of SBS-SeNR@SiO₂.

Nanogold Deposition. Gold nanoparticles were selectively deposited on the *t*-Se segments via the following process. Briefly, the collected SBS-SeNR@SiO₂ nanoparticles were redispersed into the 99% ethanol, which concentration was moderately adjusted for gold deposition. Afterwards, the equal volume of 0.5 wt% HAuCl₄/EtOH solution was added to react with SBS-SeNR@SiO₂ nanoparticles at 4 °C for 10 min. The resulting nanoparticles were washed and purified with ethanol by centrifugation.

***t*-Se Removal.** To precisely control the *t*-Se removal, the amount of sodium silicate solution was empirically decreased to 0 and 50 μL for preparing solid and hollow types of SBS-SeNR@SiO₂ nanoparticles, respectively. The freshly obtained nanofloats were transferred to another bottle containing deionized water for 6 h of aging process. Afterwards, these nanofloats were collected and transferred to ethanol. Subsequently, 100 μL of solution containing nanofloats was mixed with 300 μL of 1 M N₂H₄/THF. The mixture was sealed and shaken vigorously for 12 h (24 h for fully removing of Se core). At the end of reaction, the collected nanoparticles were washed and purified with ethanol by centrifugation.

Characterization. The morphologies and localized chemical analyses of the samples were examined by using transmission electron microscope equipped with an energy dispersive X-ray spectrometer (EDS) operating at 200 kV (JEOL, JEM-2010).

Simulation Method. The simulations were done by using VASP simulation package.² Electron wave functions were expanded in plane wave with 400 eV energy cut off in conjunction with pseudopotential by projected augmented wave (PAW) method.³ Perdew-Burke-Ernzerhof (PBE) exchange correlation functionals⁴ and a gamma centered $2 \times 3 \times 1$ Monkhorst-Pack⁵ K-point mesh were applied in calculations with Se (010) surface slab model. The Se (010) surface slab (t -Se) was composed by a $3 \times 2 \times 4$ supercell with a 20 Å vacuum inserted into the 3rd direction. The conventional c , a , b axes were corresponding to the 1st, 2nd, and 3rd simulation model vectors. The bottom $2\frac{1}{3}$ layers were fixed at the perfect bulk structure; only the top $1\frac{2}{3}$ layers were free for optimization. According to the fast Fourier transform (FFT) image, t_q -Se segment showed reflection-forbidden spots corresponding to (001) and (002), which lowered the symmetry of primitive selenium along c axis.¹ Hence, the t_q -Se surface was prepared by optimizing the slab model of removing top two rows of Se atoms (along a , 4 atoms in total). The optimal t_q -Se surface displayed some significant reconstruction on its top layer, but much minor deformation in its 2nd layer. The optimal bulk lattice constants are $a = b = 4.517$ Å, $c = 5.053$ Å. Other important parameters are given in the following table:

ENCUT	400 eV
ISMEAR	0
SIGMA	0.1 eV
PREC	Normal
EDIFF	2E-5 eV
EDIFFG	-0.01 eV/Å

Simulation Results. The adsorption energy of MPTMS molecule(s) bonding to t -Se and t_q -Se surfaces is calculated by the following equations:

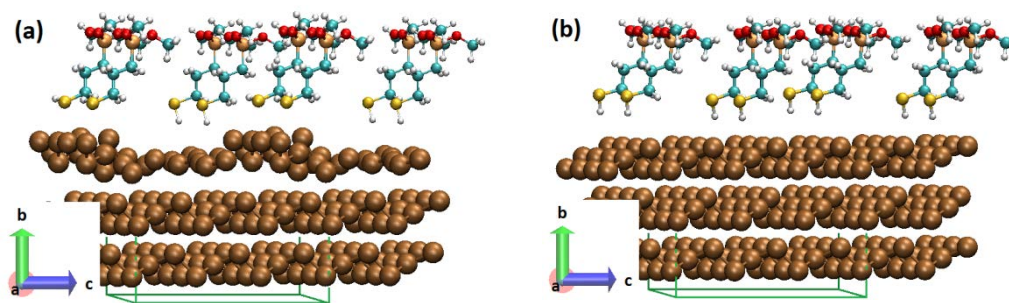
$$E_{ads} = E_{total} - E_{surf} - m * E_{MPTMS} + n * E_{H_2}. \quad (1)$$

E_{total} is the total energy of system with MPTMS monomer(s)/dimer bonding on Se surfaces. E_{surf} is the total energy of t -Se or t_q -Se surface. E_{MPTMS} is the total

energy of a MPTMS monomer or dimer, m is the number of molecules. E_{H_2} is the total energy of one H_2 molecule, n is the corresponding number of molecules released in the reaction. When MPTMS chemically bonded to t -Se and t_q -Se surfaces, forming -Se-S- bonds, n is 0.5 for 1 monomer bonding, 1 for 2 monomers or 1 dimer. For physical adsorption on t -Se and t_q -Se surfaces, n is 0. The adsorption energies are summarized in the following table:

MPTMS molecule	t -Se surface (eV)	t_q -Se surface (eV)
Chemical adsorption		
1 monomer	0.73	-0.67
2 monomers	0.55	-1.14
1 dimer	1.24	-0.32
Physical adsorption		
1 monomer	-0.08	-0.13
2 monomers	-0.11	-0.51

Negative adsorption energy implies an endothermic reaction. Accordingly, chemical bonds (i.e., -Se-S-) are not preferred forming on t -Se surface due to the positive adsorption energies. MPTMS molecules tend to physically adsorb on t -Se surface. By contrast, it is more preferred to form the chemical bonds (-Se-S-) on t_q -Se surface with positive energy gain. The following two pictures show the optimal structures of 2 MPTMS molecules physically adsorbed on t_q -Se and t -Se surfaces.



Simulation results of 2 MPTMS monomers physically adsorbed onto the a) t_q -Se, and b) t -Se surfaces. The green box indicates the slab size for simulation. The adsorption energies for the corresponding Fig. (a) and (b) are -0.51 and -0.11 eV, respectively.

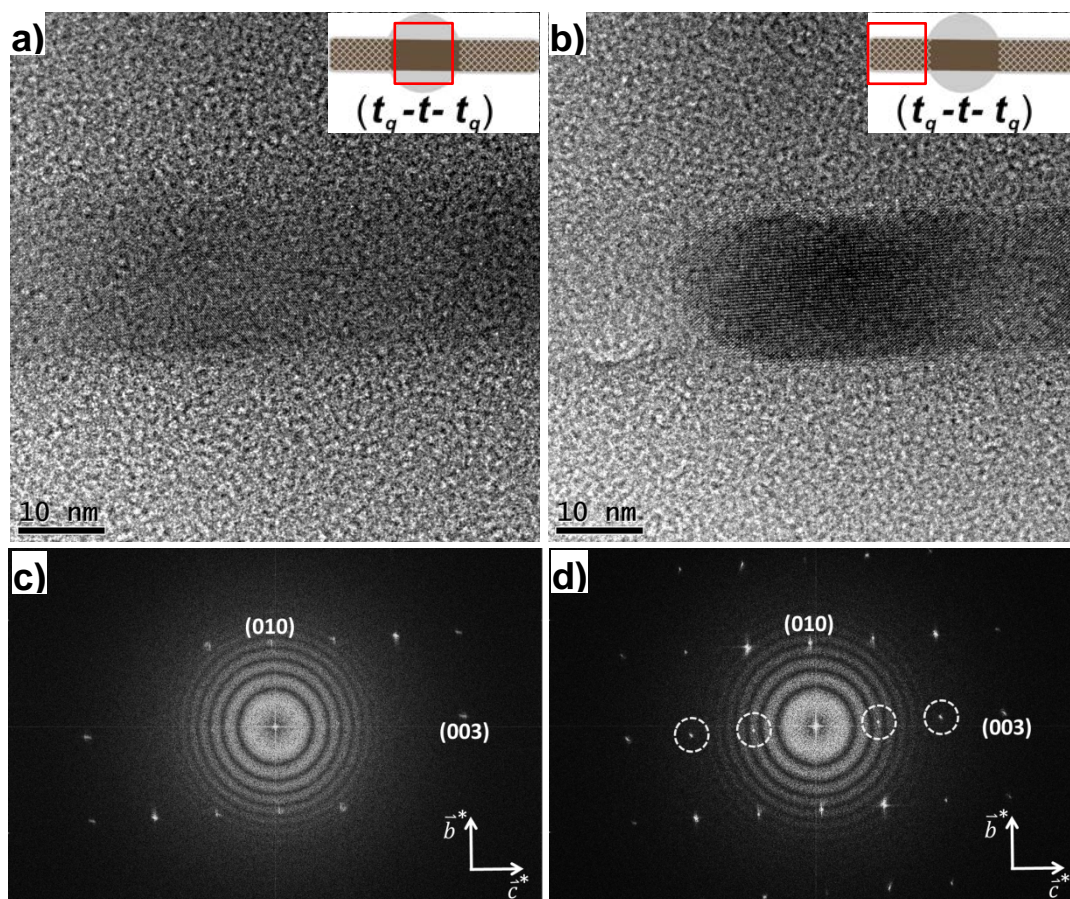


Fig. S1. HRTEM images and the corresponding fast Fourier transform patterns of a) & c) trigonal (t -Se) and b) & d) quasi-trigonal (t_q -Se) segments taken from SeNR@MPTMS particle. The space groups for trigonal and quasi-trigonal are $P3_121$ (reflection condition: $l=3n$) and $P321$, respectively. For the space group of $P321$, the (001) and (002) reflection spots can be allowed. (The red squares in the insets of image a & b indicate the taken areas of HRTEM images.)

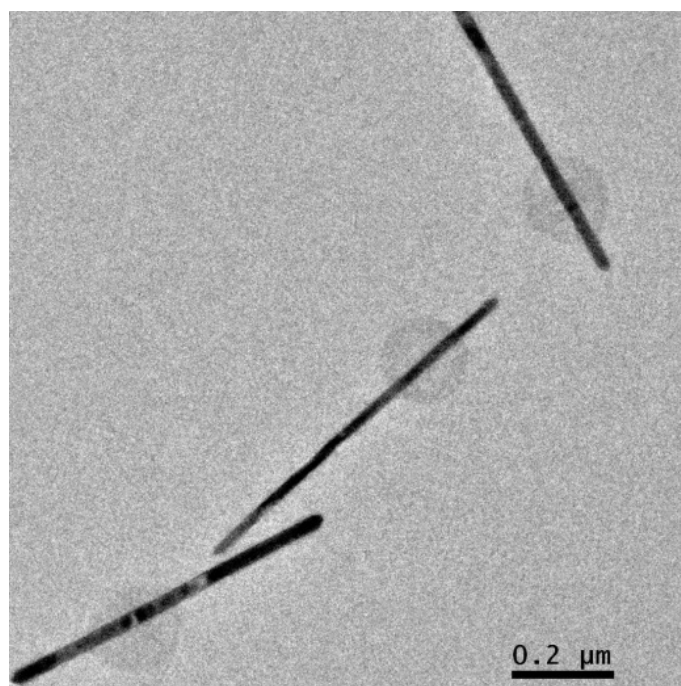


Fig. S2. TEM image of MPTMS-modified SBS-SeNRs dispersed in deionized water. These nanoparticles were modified with MPTMS molecules for 60 min.

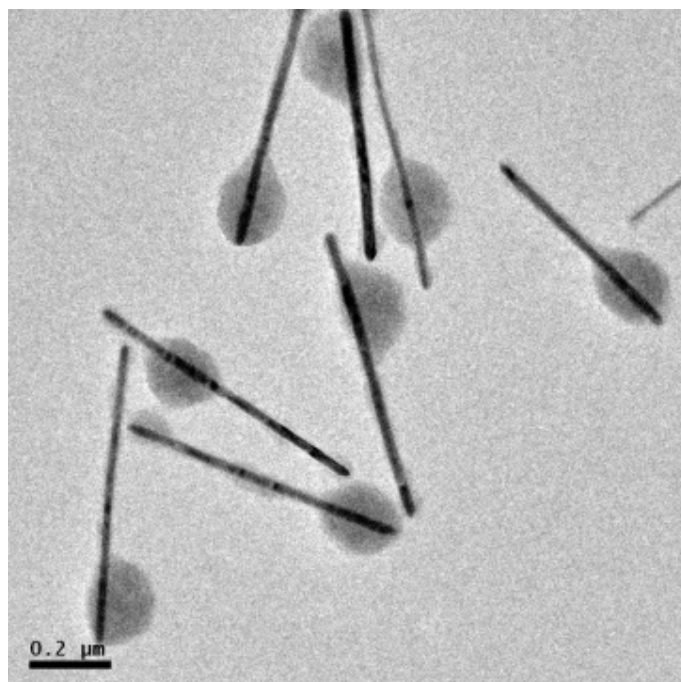


Fig. S3. TEM image of SBS-SeNR@SiO₂ nanofloats dispersed in deionized water. These nanofloats were prepared via two-step modification that SBS-SeNRs were modified with MPTMS molecules for 30 min, and further grafted with silicate for another 30 min.

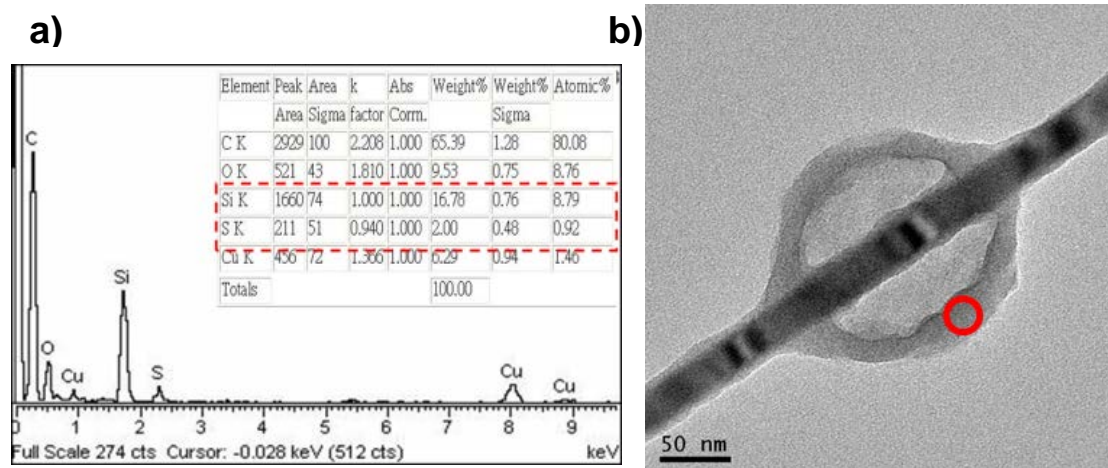


Fig. S4. Shell characterization of a) EDS analysis and b) its corresponding TEM image from hollow-type SBS-SeNW@SiO₂ nanostructures. The atomic ratio of Si to S is about 9.5, which means that the composition of shell is mainly from the condensation of silicate. (The red circle in Fig. b indicates the probing position of electron beam.)

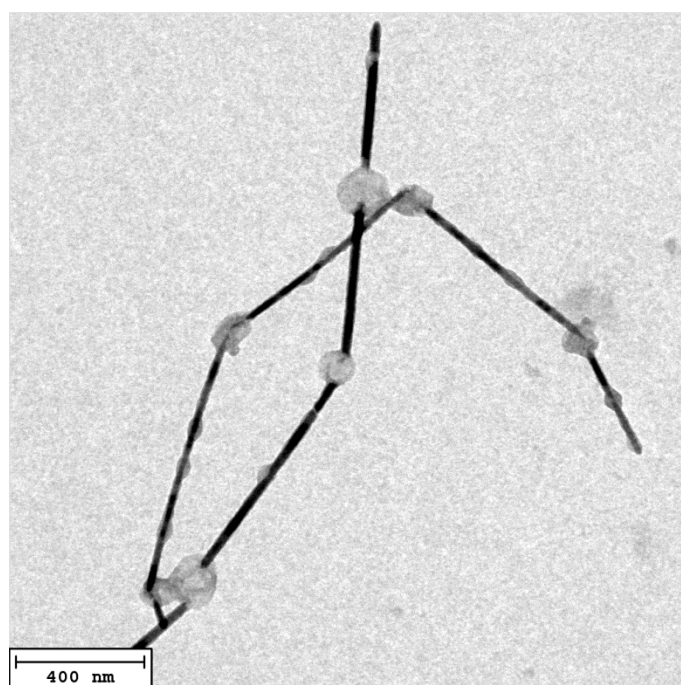


Fig. S5. TEM image of selective removal of *t*-Se segments of SBS-SeNW@SiO₂ nanostructures.

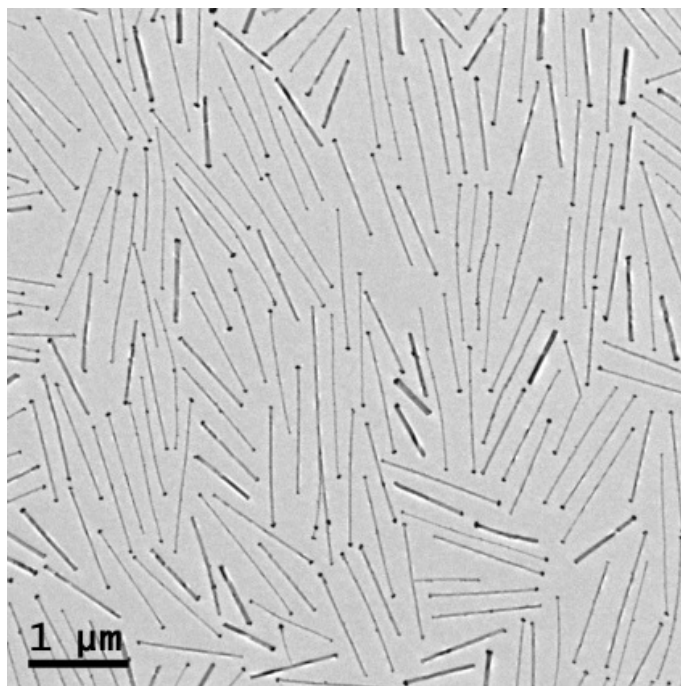


Fig. S6. TEM image of AuNPs-decorated SBS-SeNR nanostructures at 10 min of reaction time via the reduction of chloroauric acid by SBS-SeNRs.

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