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Electronic Supplementary Information

Shape and Composition Control of $Bi_{19}S_{27}(Br_{3-x}I_x)$ Alloyed Nanowires: The Role of Metal Ions

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Experimental Section

Chemicals. Iron (III) acetylacetonate ($Fe(acac)_3$, ≥99.9%), Oleylamine (OLA, 70%), oleic acid (OA, 90%), acetonitrile (99.8%) and Bis(trimethylsilyl) sulfide (TMS) were purchased from Sigma-Aldrich. Aluminum(III) acetylacetonate ($Al(acac)_3$, 99%), Aluminum(III) Chloride ($AlCl_3$, 99%) were obtained from J&K. Cobalt(III) acetylacetonate ($Co(acac)_3$), Cobalt(II) acetylacetonate ($Co(acac)_2$), Nikel(II) acetylacetonate ($Ni(acac)_2$, 95%), Iron(III) chloride ($FeCl_3$, 98%), Iron(II) chloride ($FeCl_2$, 99.5%), Bismuth(III) Bromide ($BiBr_3$, 99%), Bismuth(III) Iodide (BiI_3, 99.999%), 1-Octadecene (ODE, 90%) were obtained from Alfa Aesar. Butylamine (99%), ethanol (99.7%), isopropanol (99.7%) and n-hexane (97%) were supplied by Sinopharm chemical Reagent Co., Ltd. OLA, OA and ODE were dried under vacuum at 120 ^oC for 10 h before use.

Synthesis of $Bi_{19}S_{27}Br_3$ and $Bi_{19}S_{27}Br_3$ NWs. In a typical synthesis, 97 mg (0.3 mmol) of $Al(acac)_3$ and 180 mg (0.4 mmol) of $BiBr_3$, 400 μL of OLA, 400 μL of OA, and 4.5 mL of ODE were first loaded into a flask of 50 mL capacity. The flask was degassed by a vacuum pump for 30 min to remove water and other low-boiling point impurities at 100 ^oC and then backfilled with argon. Afterwards, The temperature was subsequently increased to 180 ^oC, 158 μL TMS and 1 mL dried ODE solution were injected and maintained at this temperature for 30 min to finish the reaction. Subsequently, the solution was cooled down to 60 ^oC and then precipitated with 10 mL of isopropanol and centrifuged at 8000 rpm for 5 min. The upper solution was discarded and n-hexane was added to disperse the nanocrystals. Then the product was further purified by adding a certain amount of isopropanol and centrifuging. This process was repeated for three times to yield the nanocrystal product that could be dispersed in common organic solvents such as toluene for later use.

Synthesis of $Bi_{19}S_{27}I_3$ NWs was carried out under otherwise identical conditions to $Bi_{19}S_{27}Br_3$ NWs, while using BiI_3 as Bi precursor.

Synthesis of $Bi_{19}S_{27}(Br_{3-x}I_x)$ alloyed NWs.

The $Bi_{19}S_{27}(Br_{3-x}I_x)$ NWs were synthesized following similar procedures as the $Bi_{19}S_{27}Br_3$ NWs by replacing $BiBr_3$ with BiI_3 partly or wholly, where the overall amount of $BiBr_3$ and BiI_3 remain stoichiometric.

Characterization

X-ray diffraction (XRD) analyses were performed on a Rigaku RINT D/Max- 2500 powder diffraction system using Cu Kα radiation source (λ = 1.541 Å) operating at 40 kV and 200 mA with a scaning rate of 5°/ min in the 2θ range of 20-70° at a step size of 0.02 s. Raman spectra of the as-synthesized NWs were obtained on Renishaw inVia confocal Raman spectrometer (λ=532 nm). The morphological characterization of the NWs were tested by scanning electron microscopy (SEM) (FEI Quanta200F scanning electron microscope). The TEM images showing the morphology of the NWs were obtained on a FEI TECNAI G^2 spirit microscope, operating at an accelerating voltage of 100 kV. HRTEM images were obtained with a FEI TECNAI F30 S-Twin (FEI company) with an accelerating voltage of 300 kV. Element analysis as an ensemble measurement was conducted on FEI Quanta 200F scanning electron microscope equipped with energy dispersive spectroscopy (EDS) detector. UV-vis-NIR diffuse-reflectance spectroscopy (DRS) spectra of $Bi_{19}S_{27}(Br_{3-x}I_x)$ alloyed NWs were acquired from a Cary 5000 spectrophotometer. X-ray photoelectron spectroscopy (XPS) were recorded on a Thermo ESCALAB 250Xi spectrometer with a Al Kα (hυ=1486.6 eV) radiation source, using C 1s (284.6 eV) as reference. Transient photocurrent measurements were conducted in a quartz cell under nitrogen in aqueous solution with 0.01 M $Eu(NO_3)_3$ /0.1 M KCl using a 300 W Xe lamp illumination. A saturated calomel electrode (SCE) was employed as the reference electrode, and a Pt foil as counter electrode. The nanocrystal film was sprayed onto FTO to form the work electrode. The photoelectrochemical response of the $Bi_{19}S_{27}(Br_{3-x}I_x)$ NWs films was obtained by varying the bias potentials from -0.5~0.6V, and the stability of the NW films was assessed by measuring the photoelectrochemical response under constant bias of 0 V under 20 s on/off chopped illumination.

Fabrication of photodetectors

In order to fabricate the $Bi_{19}S_{27}(Br_{3-x}I_x)$ (x = 0, 1, 2, 3) nanowires network-based photodetectors, the $Bi_{19}S_{27}(Br_{3-x}I_x)$ nanowires were directly dispersed on pre-prepared Au electrode pairs (50 nm thick) on SiO_2 (300 nm)/p^+-Si substrate. The electrode pairs had a channel length of 8 μm and were fabricated by photolithography (MJB4, SUSS MicroTec) and sequentially electron beam deposition (PVD 75, Kurt J. Lesker Company) and lift-off. After nanowires dispersion, the devices were annealed at 280 ^oC for 60 min to remove the residual solvent and improve the electrical contact between nanowire network and electrodes. The photoresponse properties of the photodetectors were characterized using a semiconductor characterization system (4200-SCS, Keithley) assisted by a

probe station (M150, Cascade). A Xe lamp (CEL-HXF300) was used as the white light source with a light intensity of 60 mW/cm^2.

Table S1. Atomic composition obtained by EDS overview spectra from $Bi_{19}S_{27}(Br_{3-x},I_x)$ NWs.

$Bi_{19}S_{27}(Br_{3-x},I_x)$	Bi/S/Br/I/ molar ratio	
	In precursors	In products
$Bi_{19}S_{27}Br_3$	4.00/7.50/4.00/0.00	19.00/25.97/6.62/0.00
$Bi_{19}S_{27}(Br_2,I)$	4.00/7.50/3.00/1.00	19.00/25.60/4.63/2.54
$Bi_{19}S_{27}(Br,I_2)$	4.00/7.50/2.00/2.00	19.00/25.44/2.22/4.78
$Bi_{19}S_{27}I_3$	4.00/7.50/0.00/4.00	19.00/25.91/0.00/5.73

Table S2. Comparison of experimental and simulated XRD results of hexagonal $Bi_{19}S_{27}I_3$ NWs.

h	*k*	*l*	d_{obs}	d_{calc}	d_{obs}-d_{calc}	I	2-TH
1	1	0	7.8597	7.8270	0.0327	5	11.296
2	0	0	6.7843	6.7781	0.0062	7	13.051
2	1	0	5.1238	5.1238	0.0000	10	17.293
3	0	0	4.5265	4.5187	0.0078	10	19.630
3	1	0	3.7603	3.7600	0.0003	100	23.644
2	0	1	3.4642	3.4616	0.0026	1	25.714
4	0	0	3.3921	3.3890	0.0031	0	26.275
2	1	1	3.1668	3.1659	0.0009	7	28.164
3	2	0	3.1125	3.1100	0.0025	5	28.680
3	0	1	3.0067	3.0062	0.0005	9	29.694
4	1	0	2.9602	2.9582	0.0020	20	30.186
2	2	1	2.8068	2.8063	0.0005	10	31.863
3	1	1	2.7484	2.7481	0.0003	3	32.557
5	0	0	2.7138	2.7113	0.0025	2	33.011
3	3	0	2.6118	2.6088	0.0030	1	34.345
4	0	1	2.5942	2.5928	0.0014	2	34.565
4	2	0	2.5630	2.5619	0.0011	8	34.996
3	2	1	2.4616	2.4614	0.0002	2	36.475
5	1	0	2.4356	2.4347	0.0009	4	36.887
5	0	1	2.2493	2.2490	0.0003	2	40.060
4	3	0	2.2292	2.2286	0.0006	3	40.441
5	2	0	2.1714	2.1708	0.0006	32	41.568
5	1	1	2.0835	2.0835	0.0000	4	43.396
0	0	2	2.0117	2.0133	-0.0016	2	44.991
6	0	1	1.9708	1.9704	0.0004	1	46.025
4	3	1	1.9708	1.9487	0.0221	1	46.537
1	1	2	1.9498	1.9498	0.0000	2	46.540
5	2	1	1.9106	1.9108	-0.0002	5	47.548
6	2	0	1.8801	1.8799	0.0002	4	48.378
2	1	2	1.8755	1.8737	0.0018	1	48.546
6	1	1	1.8391	1.8391	0.0000	0	49.523
3	0	2	1.8391	1.8390	0.0001	2	49.526
7	1	0	1.7956	1.7956	0.0000	3	50.807
2	2	2	1.7909	1.7902	0.0007	2	50.970
3	1	2	1.7736	1.7749	-0.0013	1	51.445
7	0	1	1.7449	1.7453	-0.0004	3	52.382
5	4	0	1.7359	1.7357	0.0002	2	52.692
6	3	0	1.7079	1.7080	-0.0001	1	53.616
6	2	1	1.7038	1.7034	0.0004	2	53.770
8	2	0	1.4789	1.4792	-0.0003	2	62.769
8	1	1	1.4789	1.4759	0.0030	0	62.908
5	2	2	1.4754	1.4762	-0.0008	4	62.911
6	4	1	1.4502	1.4507	-0.0005	2	64.148
9	1	0	1.4208	1.4211	-0.0003	2	65.661

Crystal date

Formula	$Bi_{19}S_{27}I_3$
Crystal system	hexagonal
Space group	P63/m(176)
Unit cell dimensions	a=b=15.6537 Å, c=4.0265 Å

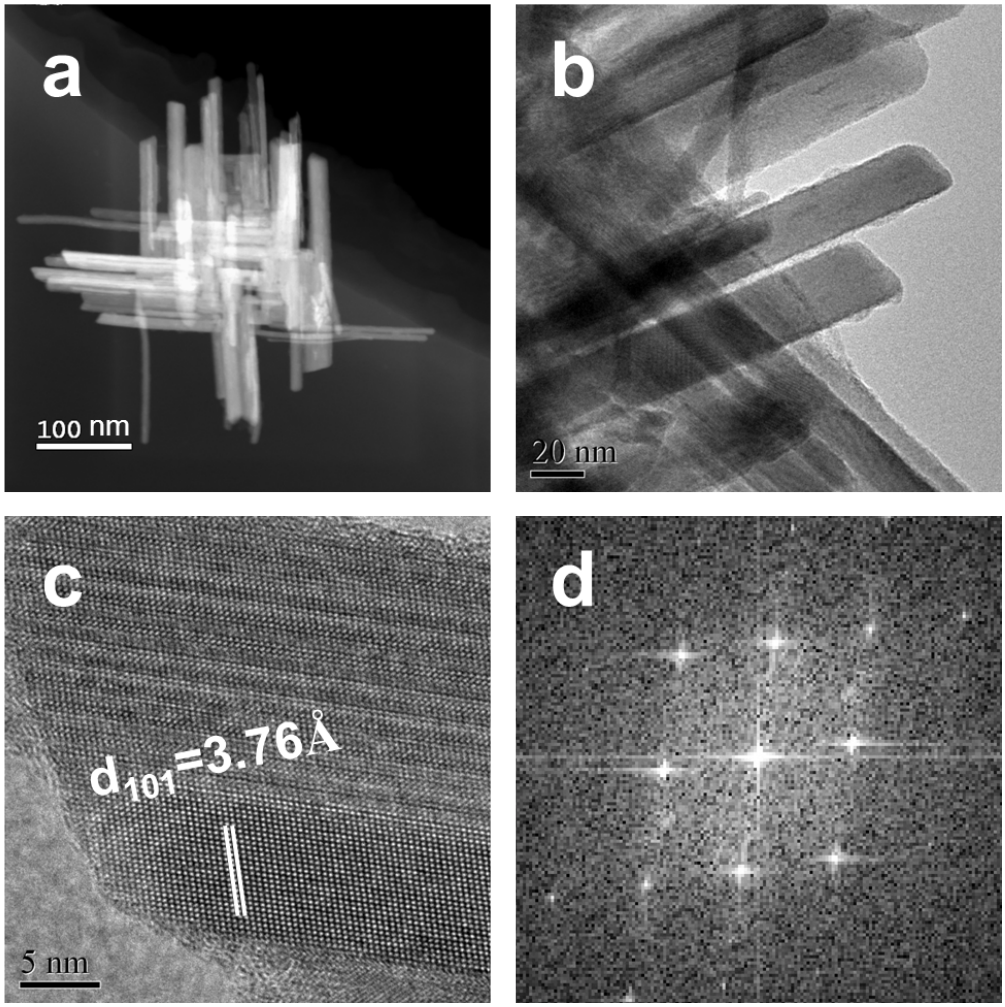

Fig. S1 HAADF-STEM image (a), TEM image (b), HRTEM image (c), and corresponding FFT pattern (d) of fabric-like Bi_2S_3 nanowires.

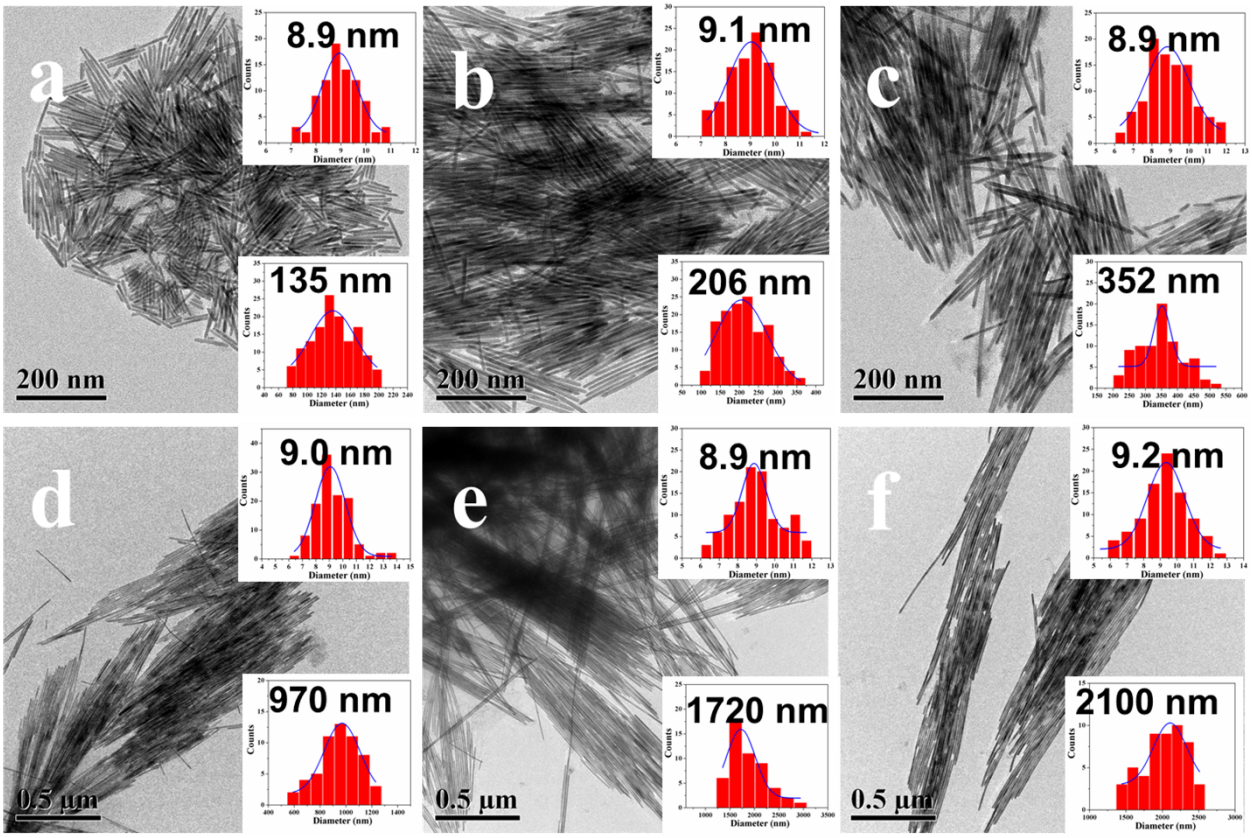

Fig. S2 TEM images and corresponding diameters (top right corner) and length distributions (bottom right corner) of $Bi_{19}S_{27}Br_3$ NWs obtained with different duration after injection of S source at 180 ^{o}C: a) instant, b) 5 min, c) 10 min, d) 30 min, e) 60 min, and f) 120 min.

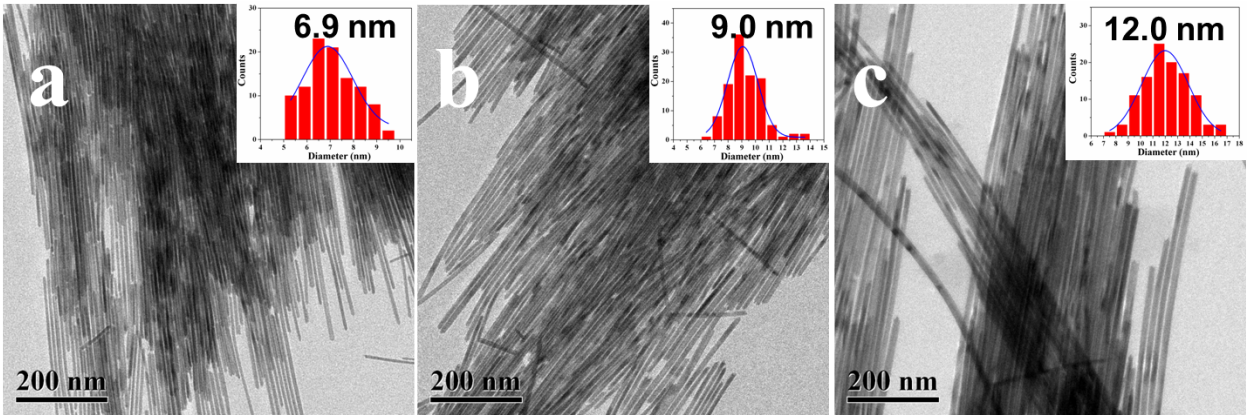

Fig. S3 TEM images and corresponding size distributions (inset) of $Bi_{19}S_{27}Br_3$ NWs obtained with different reaction temperatures (reaction time: 30 min): a) 160 °C, b) 180 °C, and c) 200 °C.

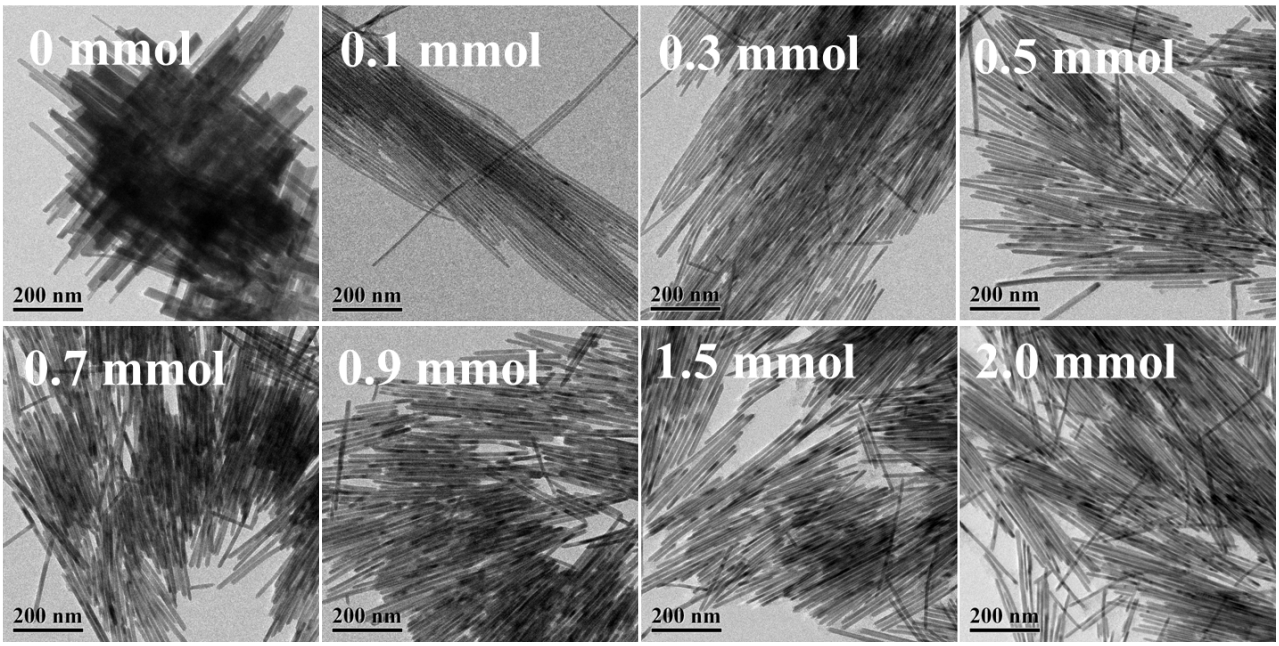

Fig. S4 TEM images of $Bi_{19}S_{27}Br_3$ NWs obtained by adding different amounts of $Al(acac)_3$.

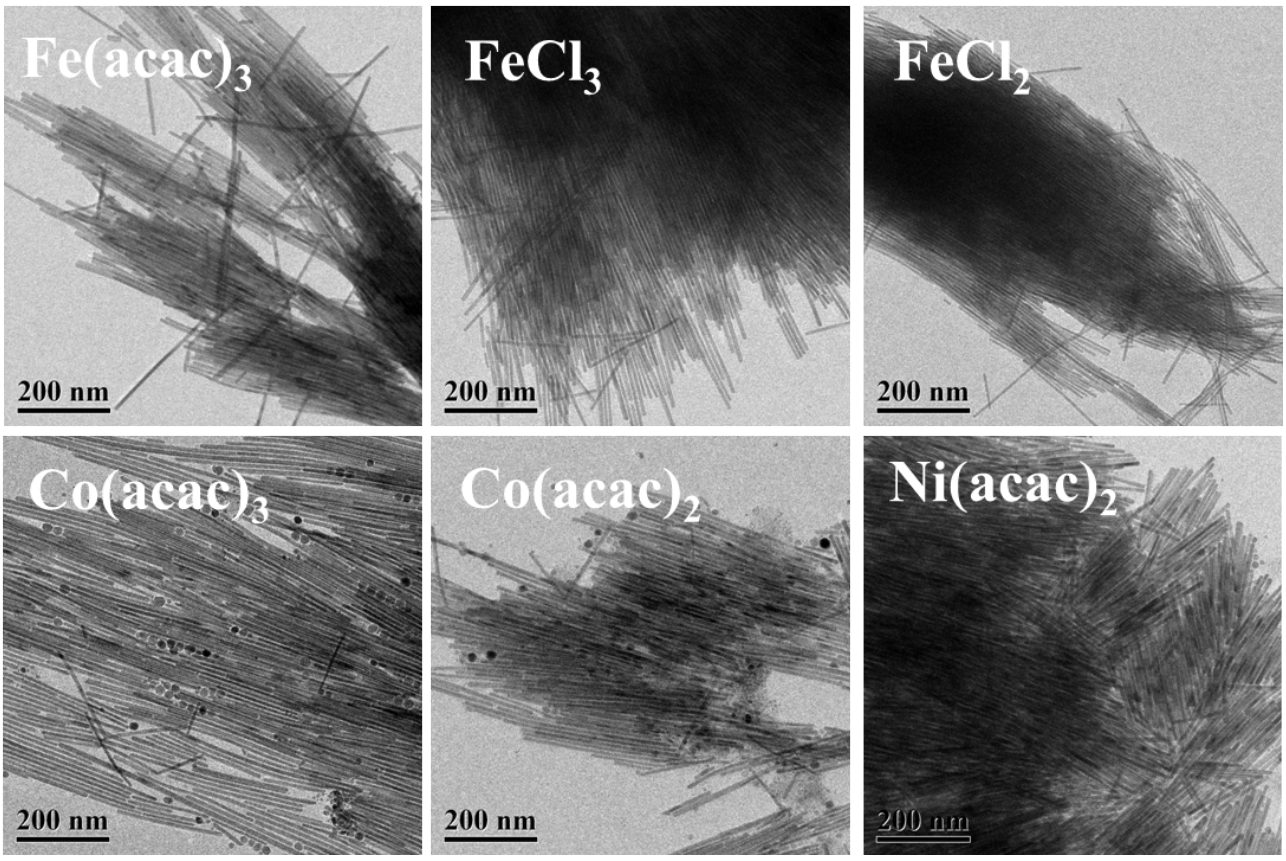

Fig. S5 TEM images of $Bi_{19}S_{27}Br_3$ NWs obtained by adding different metal salts.

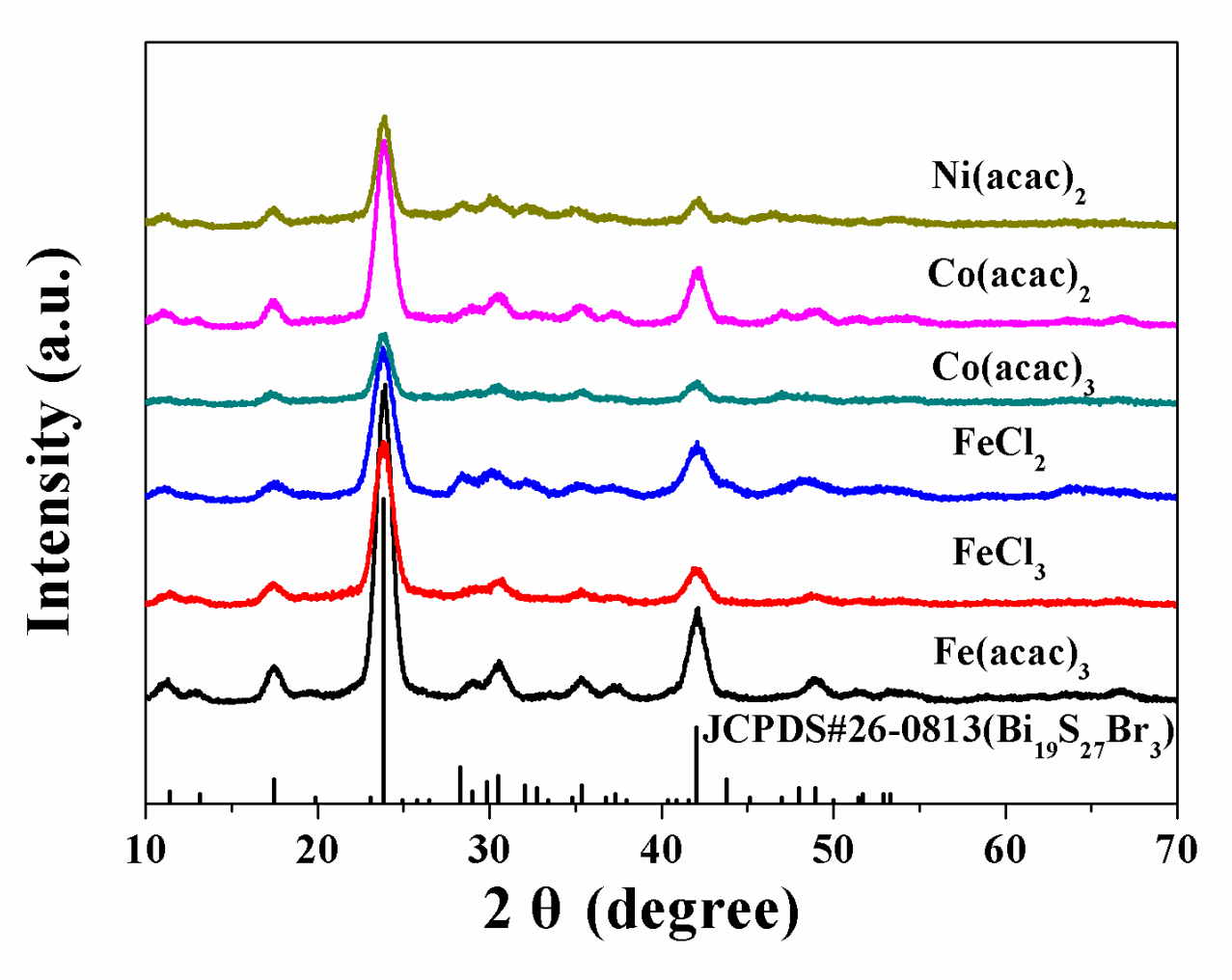

Fig. S6 XRD patterns of $Bi_{19}S_{27}Br_3$ NWs obtained by adding different metal salts.

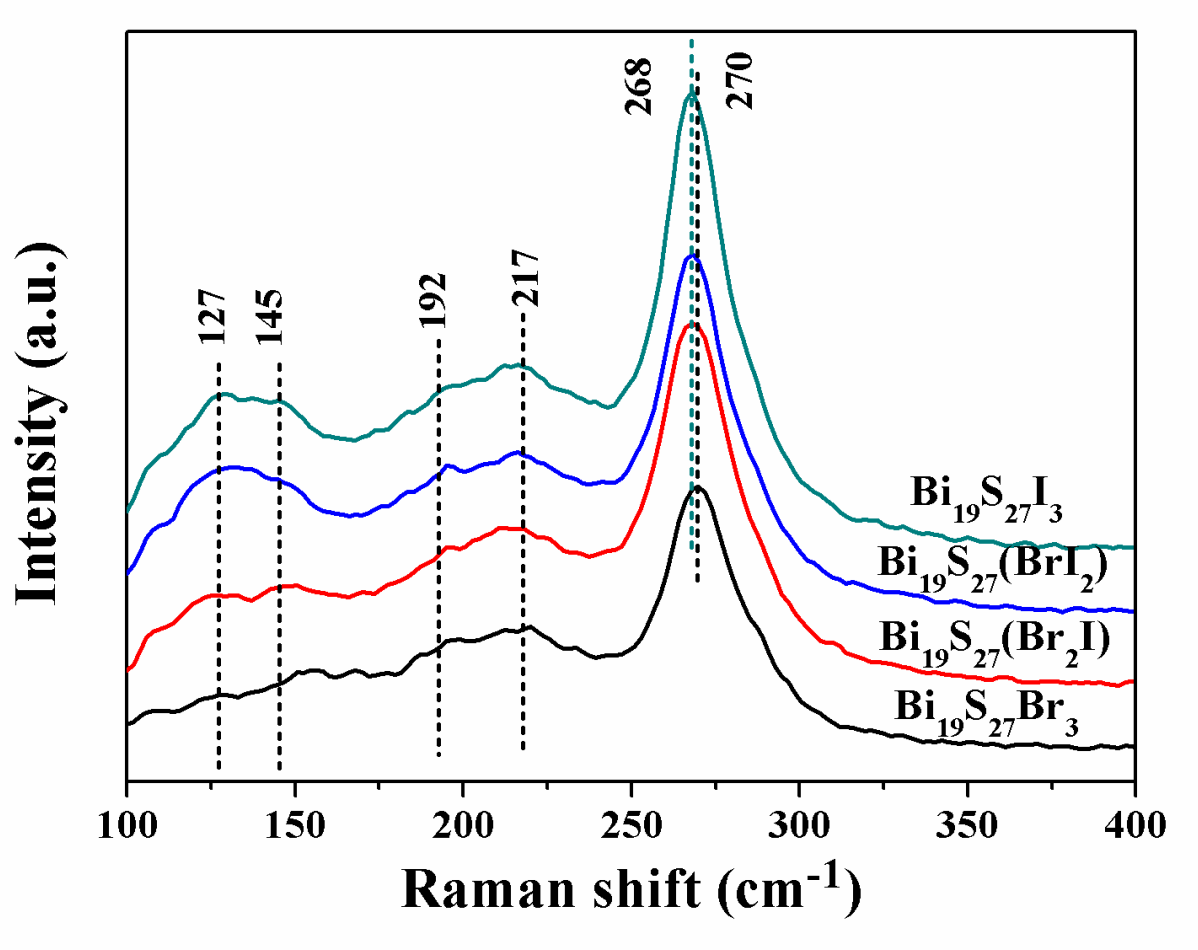

Fig. S7 Raman spectra of the $Bi_{19}S_{27}(Br_{3-x},I_x)$ NWs with various I/(Br+I) ratios ($0 \leq x \leq 3$).

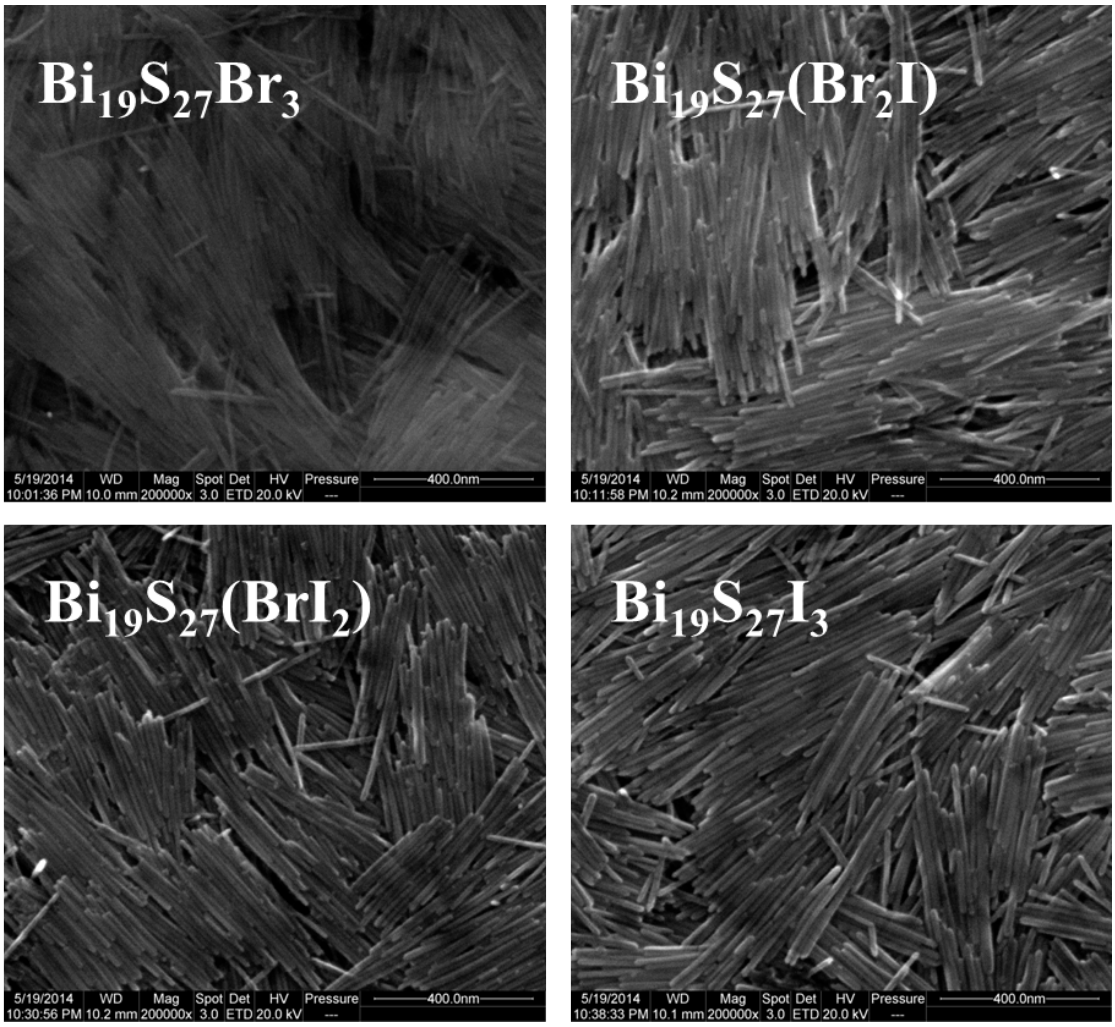

Fig. S8 SEM images of $Bi_{19}S_{27}(Br_{3-x}I_x)$ NWs with various I/(Br+I) ratios ($0 \leq x \leq 3$).

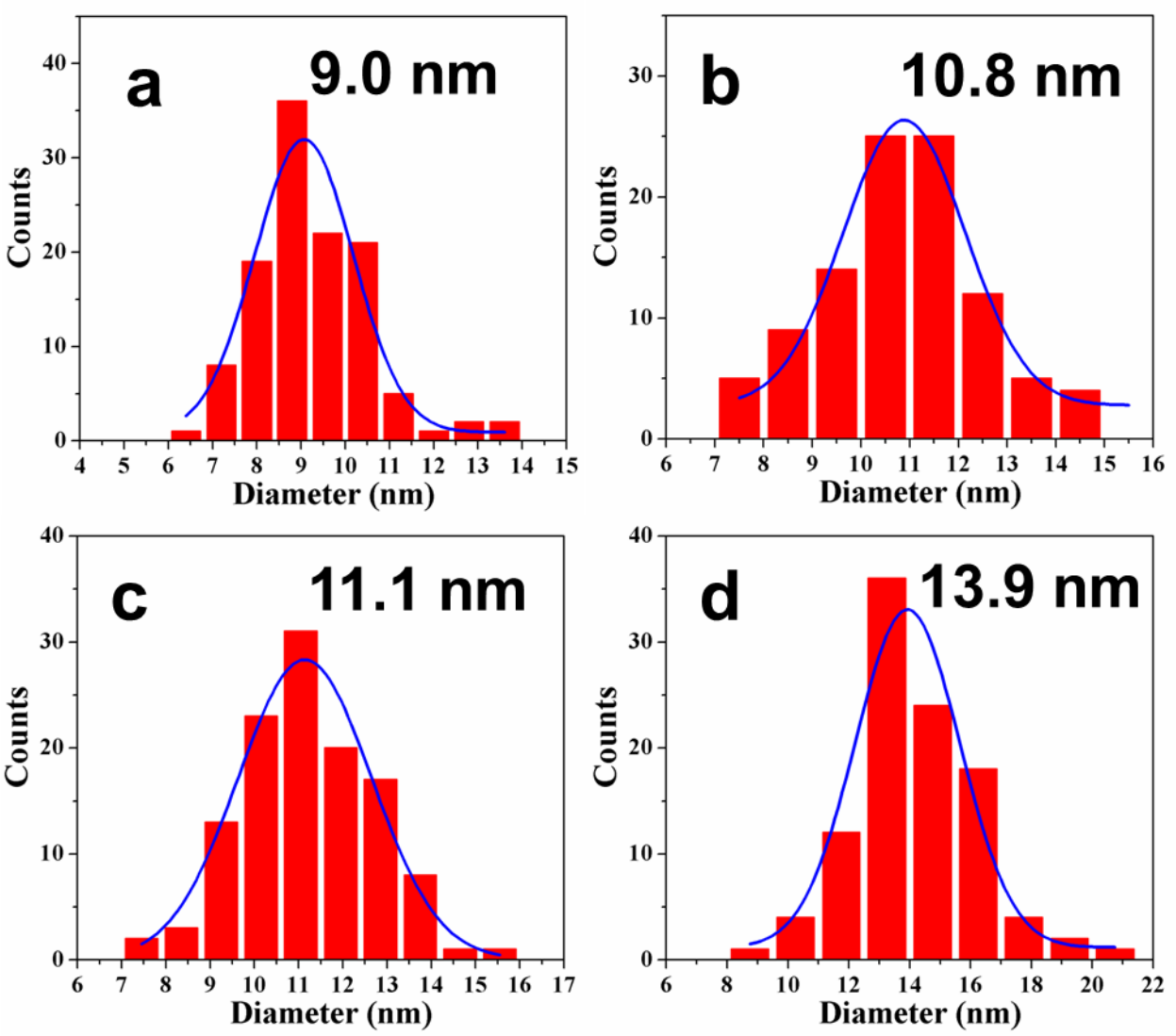

Fig. S9 The size distributions of the as-synthesized nanowires: a) $Bi_{19}S_{27}Br_3$, b) $Bi_{19}S_{27}(Br_2I)$, c) $Bi_{19}S_{27}(BrI_2)$, and d) $Bi_{19}S_{27}I_3$.

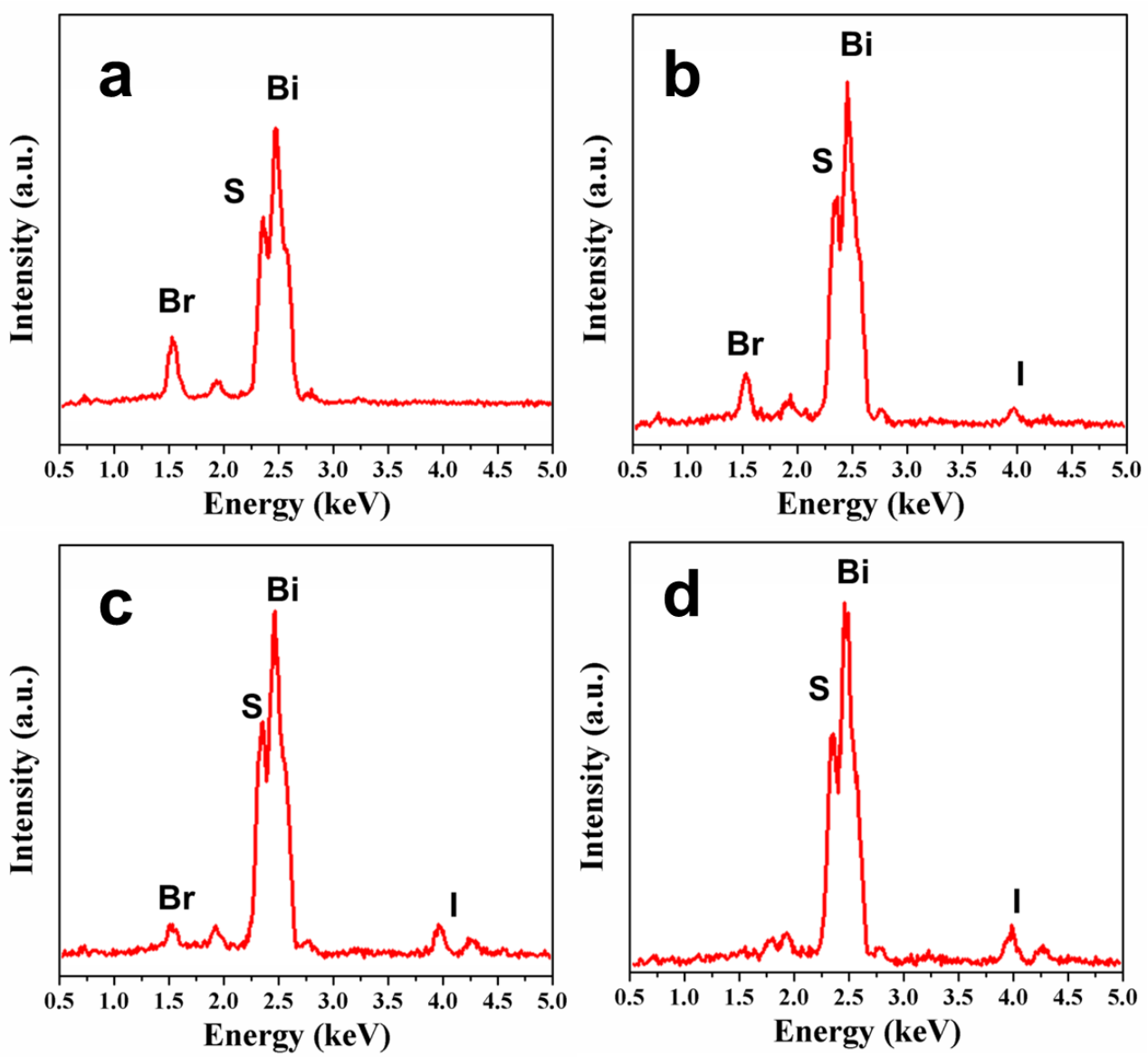

Fig. S10 EDAX spectra of the as-synthesized nanowires: a) $Bi_{19}S_{27}Br_3$, b) $Bi_{19}S_{27}(Br_2I)$, c) $Bi_{19}S_{27}(BrI_2)$, d) $Bi_{19}S_{27}I_3$.

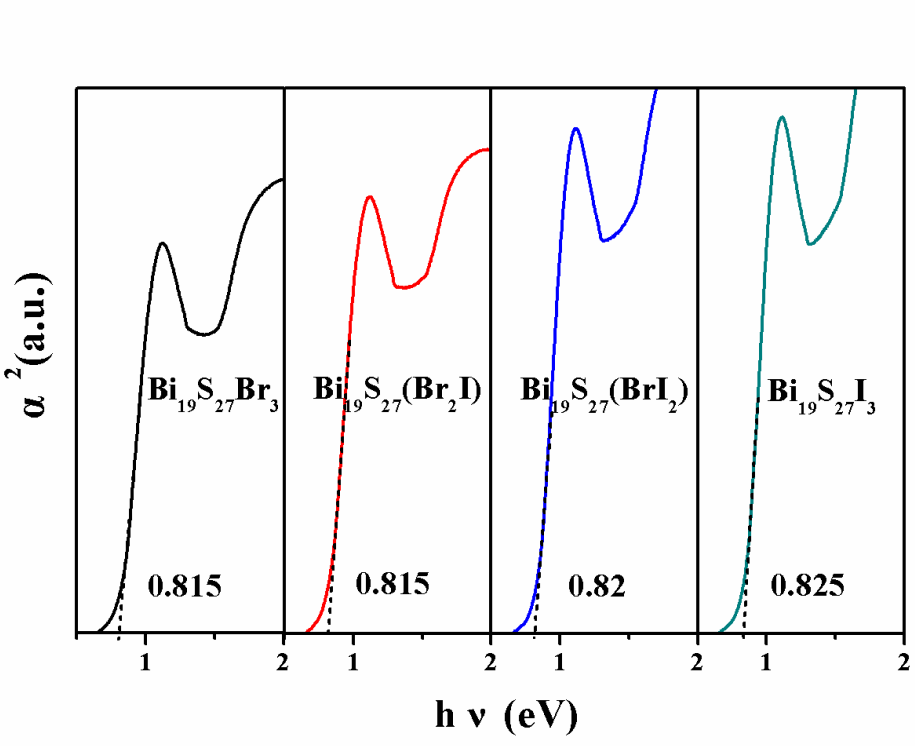

Fig. S11 Band gaps of the $Bi_{19}S_{27}(Br_{3-x},I_x)$ NWs with various I/(Br+I) ratios ($0 \leq x \leq 3$) derived from UV-vis absorption spectra.

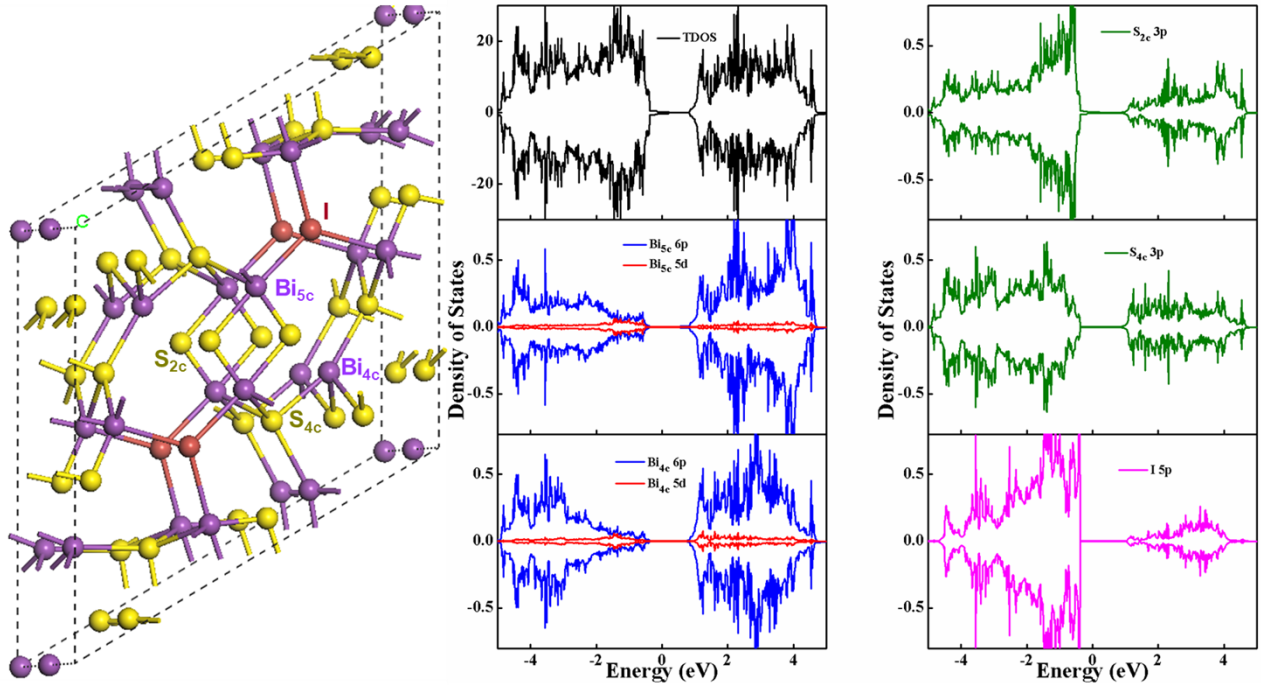

Fig. S12 The structural model and DOS for $Bi_{19}S_{27}I_3$.

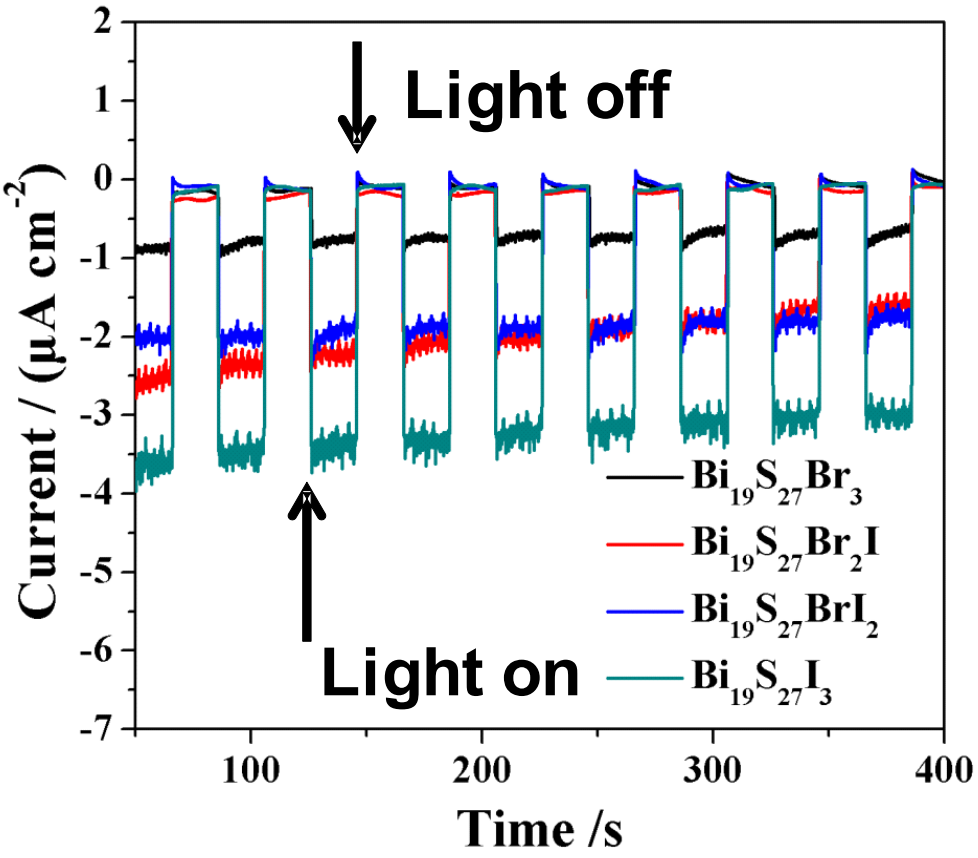

Fig. S13 Transient photocurrent response of the $Bi_{19}S_{27}(Br_{3-x},I_x)$ NWs under a constant bias of 0 V.

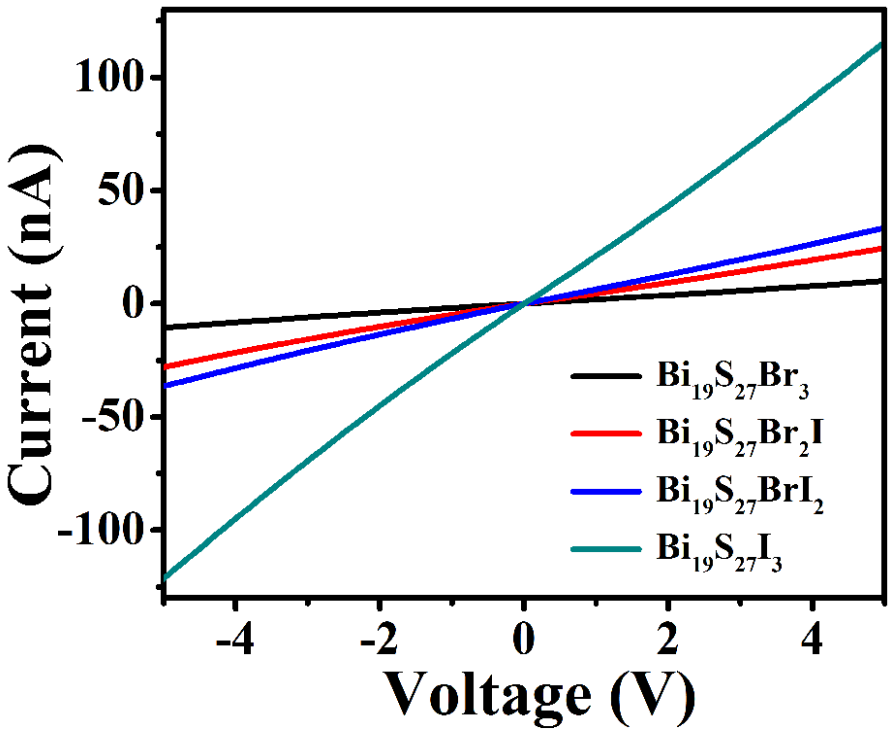

Fig. S14 *I-V* curves of the PDs based on the $Bi_{19}S_{27}(Br_{3-x}I_x)$ NW networks (x=0, 1, 2, 3) in the dark.