Electronic Supplementary Material (ESI) for CrystEngComm.

Supplementary Information

Organic bromide-assisted one-pot synthesis of Bi_2S_3 nanorods using DMSO as a sulfur supply

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1. XPS analysis of Bi_2S_3 nanorods

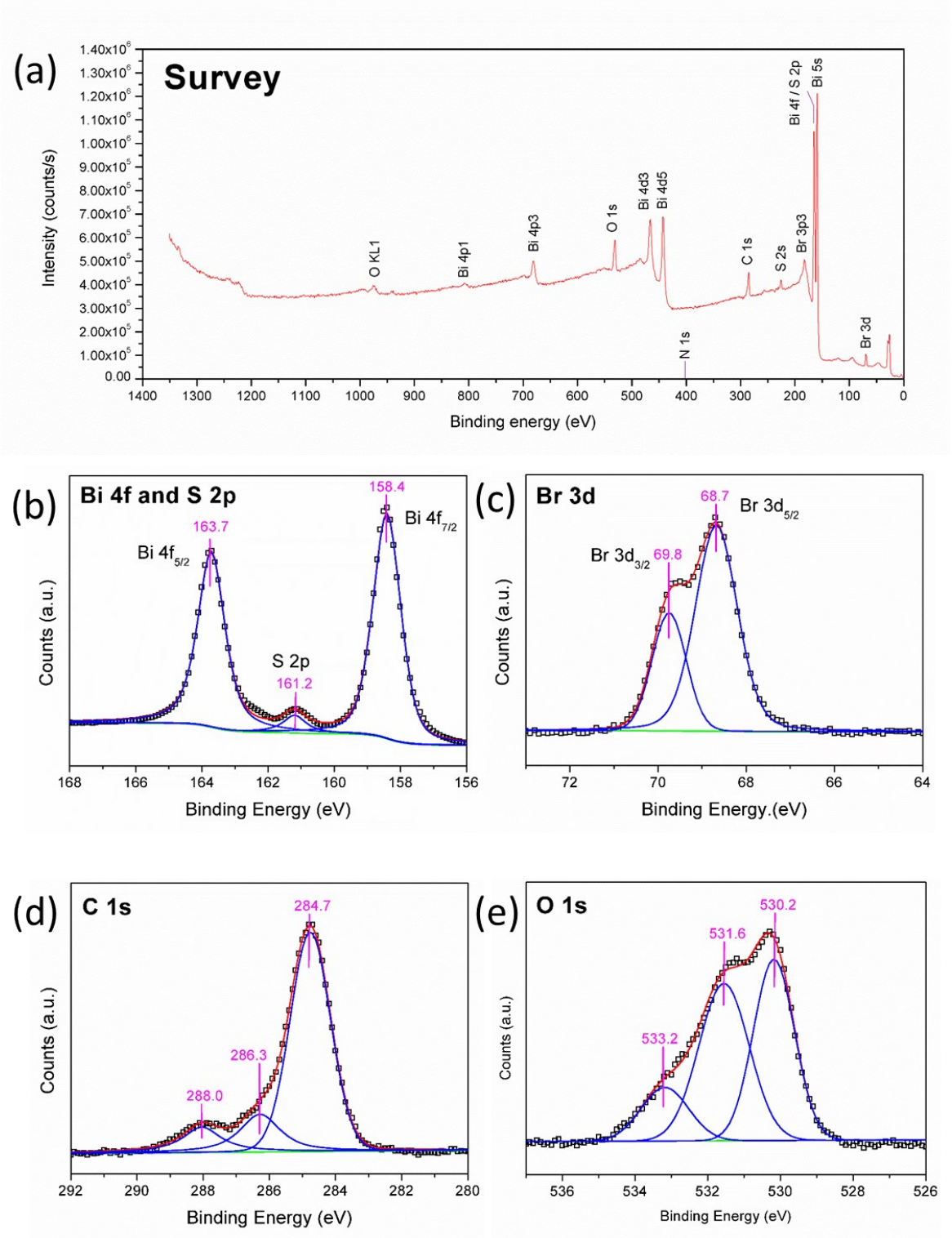

Figure S1. The XPS survey spectra of Bi_2S_3 nanorods prepared with Et_4NBr. (a) XPS survey showing the presence of C, O, and Br traces, along with the major components of Bi and S, (b-e) high-resolution XPS spectra of Bi4f / S 2p, Br 3d, C 1s, and O 1s.

Table S1. Assignment of the high resolution XPS peaks of each element

Element	Binding energy (eV)	XPS signal	Chemical bond	Ref.
Bi	158.4	Bi $4f_{7/2}$	Bi^{3+} in BiOBr	1, 2
	163.7	Bi $4f_{5/2}$	Bi^{3+} in Bi_2S_3	1
S	161.2	S 2p	-	1, 3
Br	68.7	Br $3d_{5/2}$	Free Br^-	4
	69.8	Br $3d_{3/2}$	Alkyl bromide	4, 5
C	284.7	C 1s	C-C or C=C	6
	286.3	C 1s	C-O / C-OH	6, 7, 9
	288.0	C 1s	C=O	7
O	530.2	O 1s	Chemisorbed atomic O	8
	531.6	O 1s	Lattice oxygen of BiOBr	1
	533.2	O 1s	Hydroxyl	9

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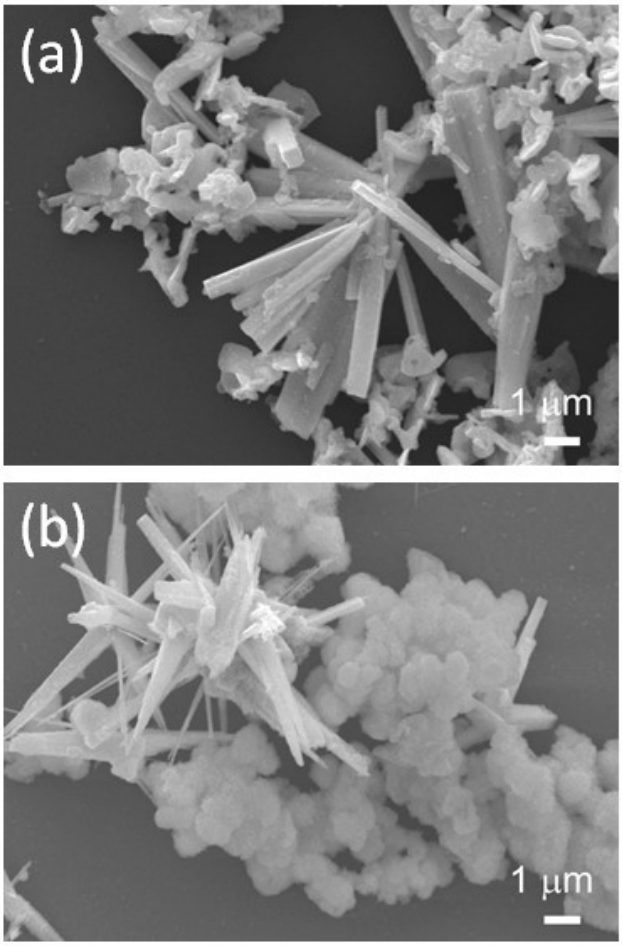

Figure S2. SEM images of Bi_2S_3 products synthesized with the use of KBr as a bromide source. Each image shows (a) microrods and (b) particulate aggregates.

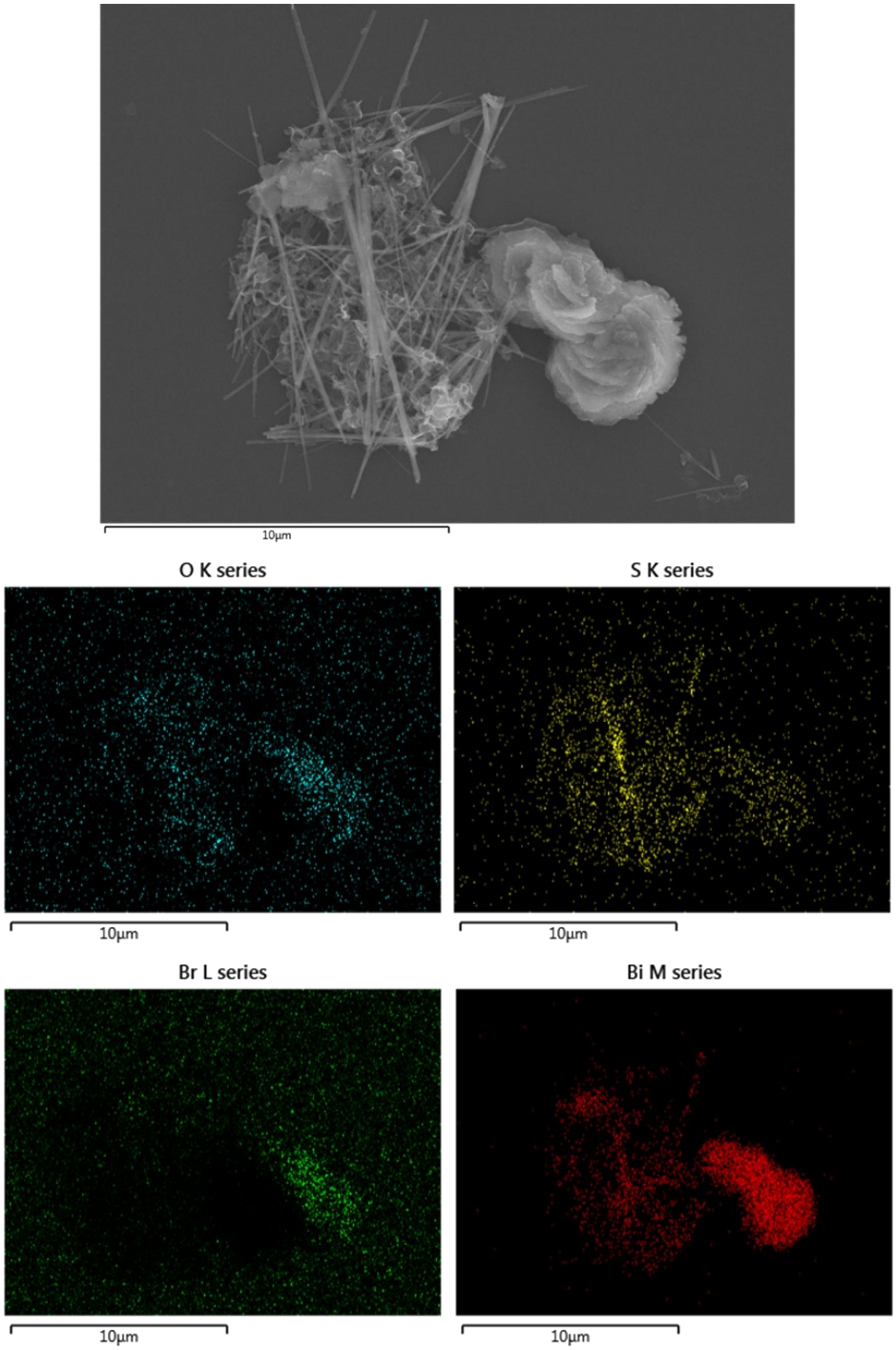

Figure S3. SEM image and corresponding atomic mapping of the BiOBr and Bi_2S_3 mixture.

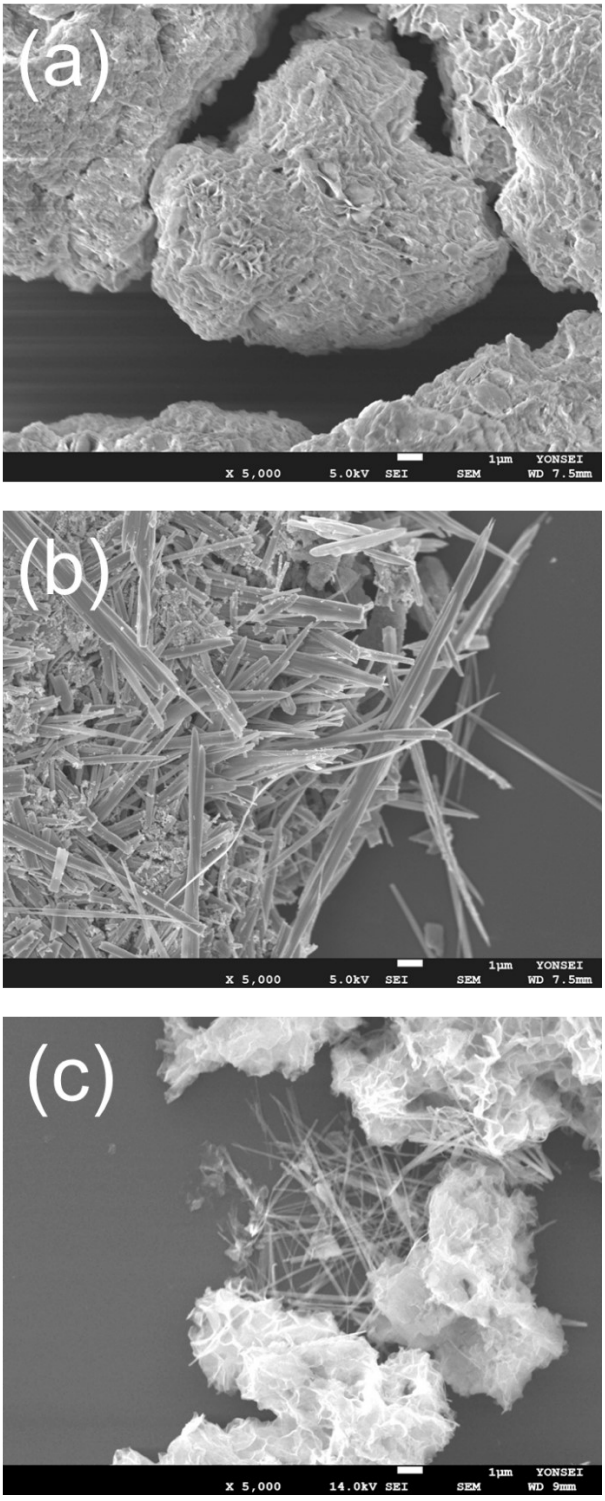

Figure S4. SEM images of Bi products prepared under various synthesis protocols (scale bars: 1 μm). (a) BiOBr prepared by Et_4NBr is reacted further with DMSO in the presence of KBr, (b) BiOBr prepared by Et_4NBr is reacted further without any bromide source, (c) Bi species prepared by KBr is reacted further with DMSO in the presence of Et_4NBr.

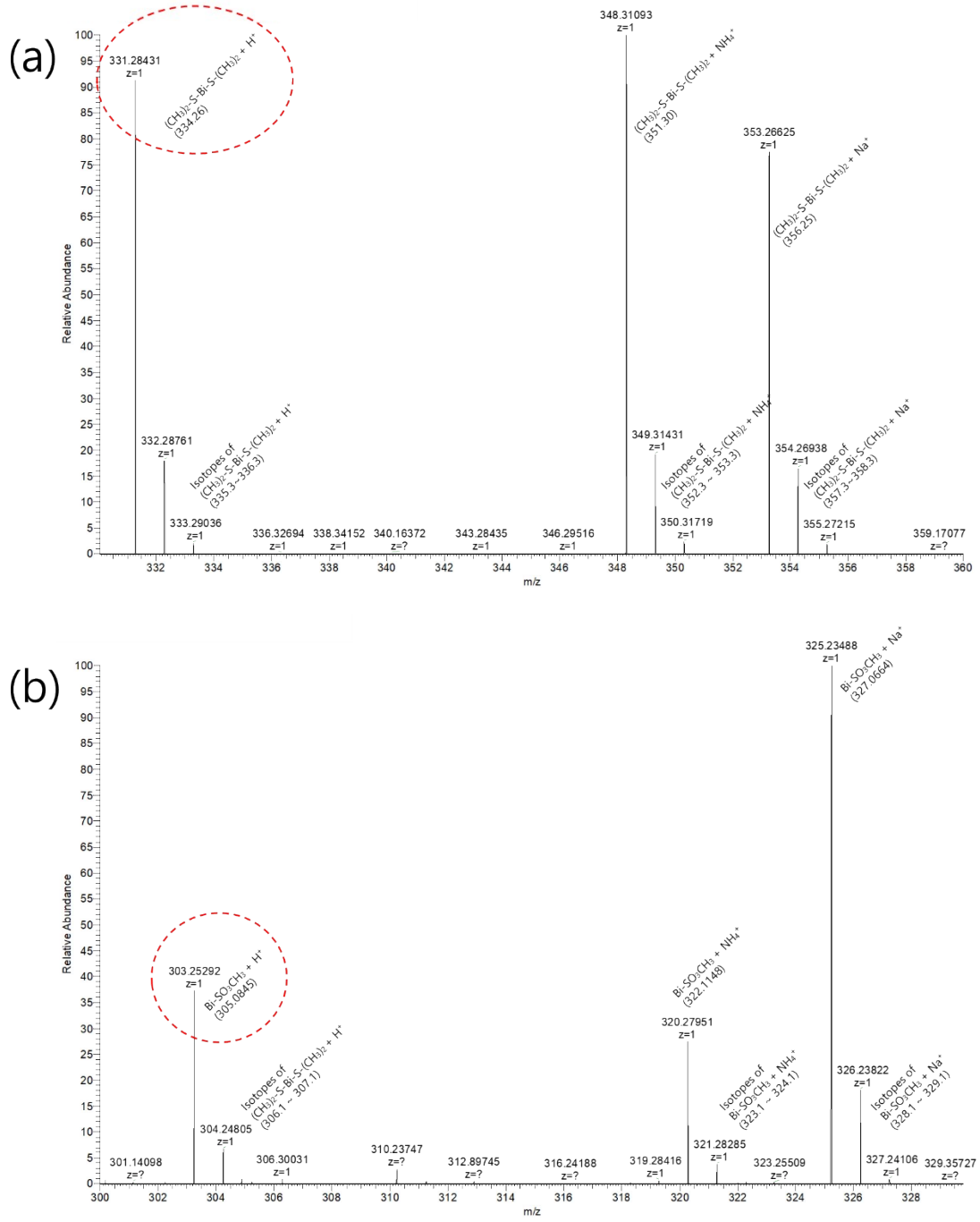

Figure S5. LC-Mass spectra of the reaction intermediates. Characteristic peaks are marked with dotted red circles. (a) m/z = 331.28 is assigned to $(CH_3)_2S$-Bi-$S(CH_3)_2$. Peaks of m/z = 348.31 and 353.27 are assigned to $(CH_3)_2S$-Bi-$S(CH_3)_2$ species combined with NH_4 and Na^+, respectively. Each peak has subordinate peaks originating from the sulfur isotopes. (b) m/z = 303.25 assigned to Bi-SO_3CH_3. Peaks of m/z = 320.28nd 325.23 are also assigned to Bi-SO_3CH_3 species combined with NH_4 and Na^+, respectively. Each peak has subordinate peaks originating from the sulfur isotopes.

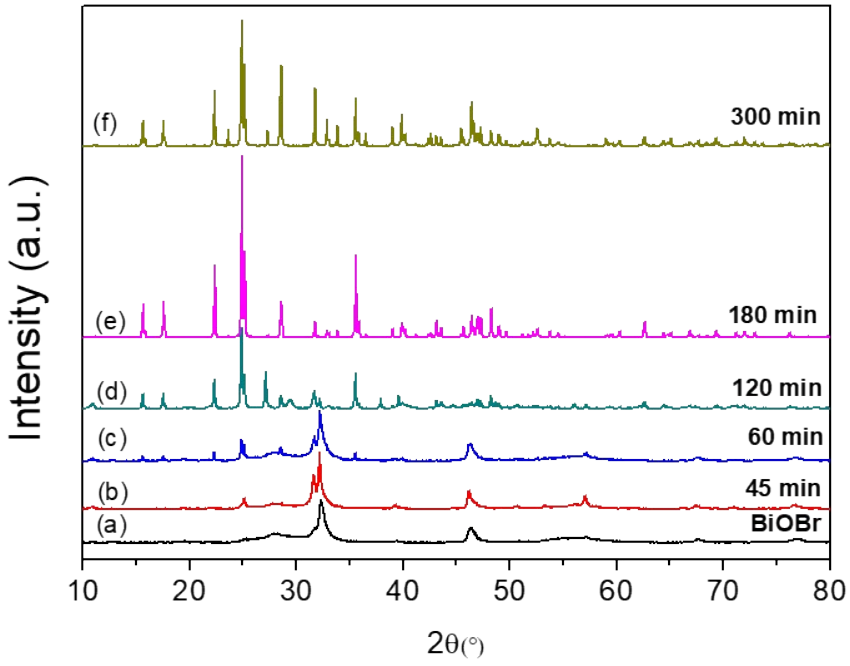

Figure S6. X-ray diffraction patterns showing the transformation of BiOBr to Bi_2S_3 with the reaction time

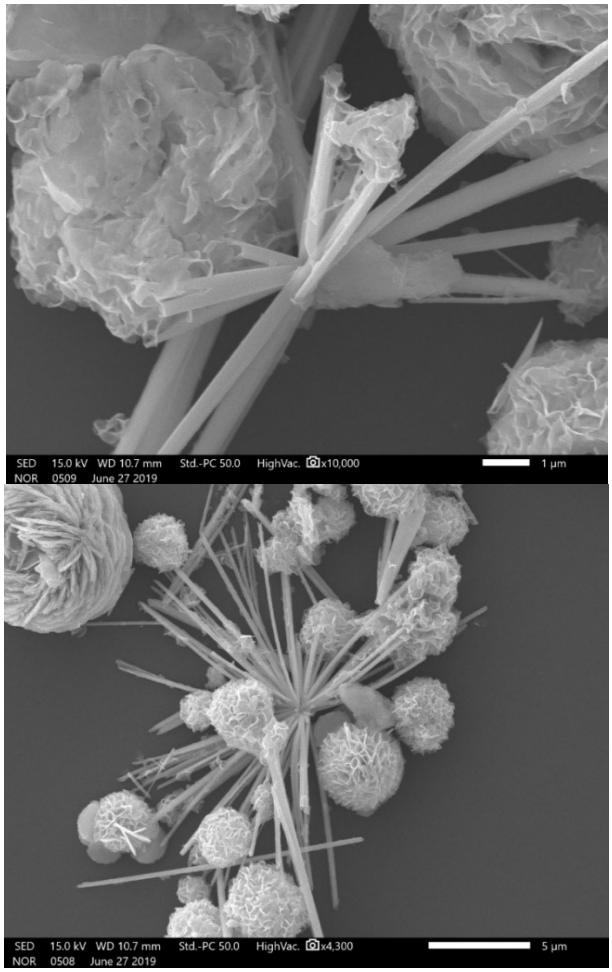

Figure S7. Radial growth of Bi_2S_3 nanorods from the BiOBr microspheres. Images were taken at different magnifications.

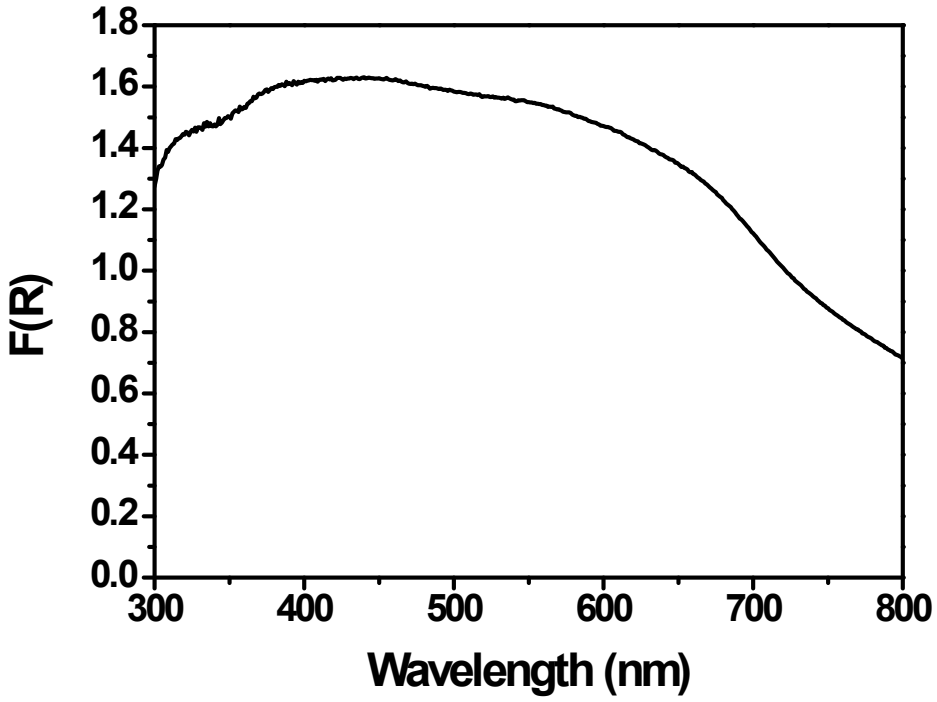

Figure S8. UV-vis-DRS absorbance spectrum of Bi_2S_3.

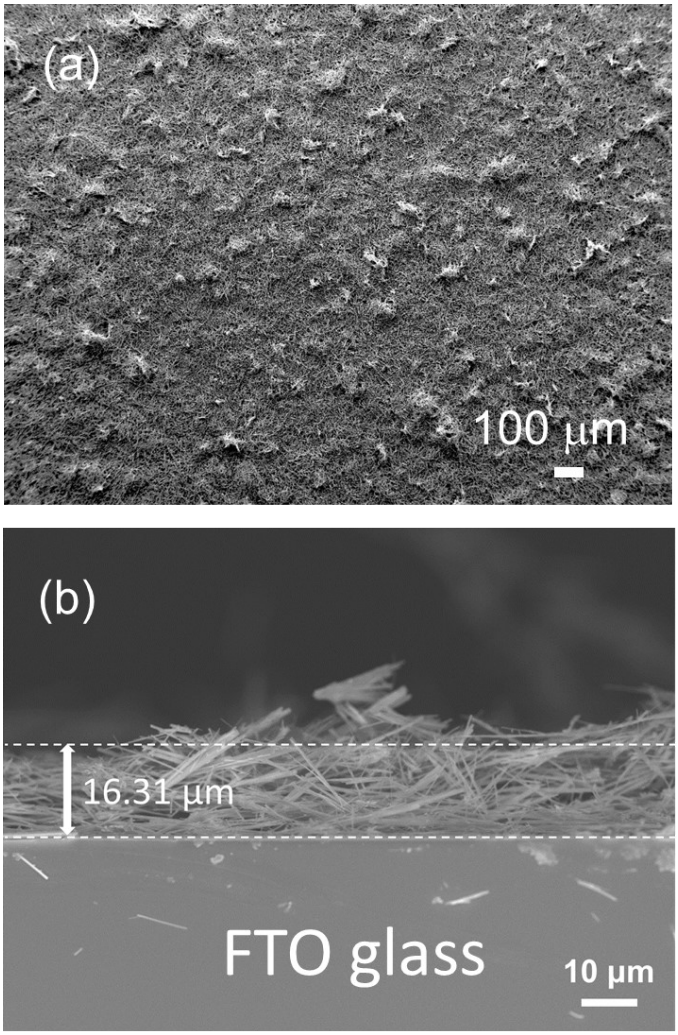

Figure S9. SEM images of the Bi_2S_3 nanorods layer deposited on the FTO glass. (a) top and (b) cross-section views.

Table S2. Comparison of the photo-response time of the Bi_2S_3 photodetectors

Morphology	Synthesis method (reaction temp., time)	Bi & S sources / Solvent*	Band gap energy (eV)	Response time (ms)	Decay time (ms)	Ref. (reference in the manuscript)
Nanotube	Aerosol assisted CVD (deposition on FTO glass)	$Bi_2[S_2CN(C_2H_5)_2]_3]_2$ / chloroform, dichloromethane	1.8	n/a	20,000~25,000	Chem. Mater. 2010, 22, 5084-5092 (Ref 3)
Nanorods (grown like a sea urchin)	Hydrothermal (150 ºC, 6 h)	$Bi(NO_3)_3•5H_2O$, thiourea / ethylene glycol, water, ethylene diamine	1.62	177	907	CrystEngComm 2013, 15, 6611-6616 (Ref 7)
Microcrystals	Solvothermal with oleic acid (180 ºC, 2 h)	$Bi(CH_3CO_2)_3$, S powder / 1-octadecene, oleic acid	1.9	500	800	RSC Adv 2012, 2, 234-240 (Ref 12)
Nanorod	Solvothermal with alkylamines (160 ºC, 1 h)	$BiCl_3$, S powder / organic amine	1.89	300-600	700-900	CrystEngComm 2017, 19, 727-733 (Ref 42)
Nanosheet	Solvothermal (180 ºC, 8 h)	Triphenyl bismuth, dibenzyldisulfide / oleylamine, ethanol, PVP	1.9	0.01	0.35	Small 2015, 11, 2848-2855 (Ref 43)
Short nanorod	Solvothermal with oleic acid (170 ºC 0.5 h + 100 ºC 2 h)	$Bi(CH_3CO_2)_3$, $[(CH_3)_3Si]_2S$ / 1-octadecene, oleic acid	1.3	~300	~300	Nano Lett. 2008, 8, 4002-4006 (Ref 44)
Nanorod	Hydrothermal (130 ºC, 9 h)	$Bi(NO_3)_3•5H_2O$, thiourea / water, $NH_3•H_2O$, EDTA	n/a	372	386	Front. Optoelectron. 2015, 8, 282-288
Nanorod	Molten salt solvent	$Bi(NO_3)_3•5H_2O$, $Na_2S•9H_2O$ / $LiNO_3$+KNO_3 (melt)	n/a	< 100	< 100	Solid State Comm. 2009, 43-44,, 1894-1896
Sea urchin-like structure	Solvothermal (60 ºC, 24 h)	$Bi(NO_3)_3•5H_2O$, thiourea / ethylene glycol, PVP	n/a	142	151	Nanoscale Res. Lett. 2015, 10, 286
Sea urchin-like structure	Hydrothermal (120 ºC, 6 h)	$Bi(NO_3)_3•5H_2O$, thiourea / water	n/a	50	240	RSC Adv. 2012, 2, 6258-6261
Nanorod	Solvothermal (180 ºC)	$Bi(NO_3)_3•5H_2O$ / DMSO, Et_4NBr	1.5	920	9700	This work

*Major solvent is written in blue. Other additives including capping agents are writtem in green