Electronic Supplementary Information

Solution-based synthesis of nanocrystalline $KBiS_2$ films at low temperatures and study of photoinduced charge generation

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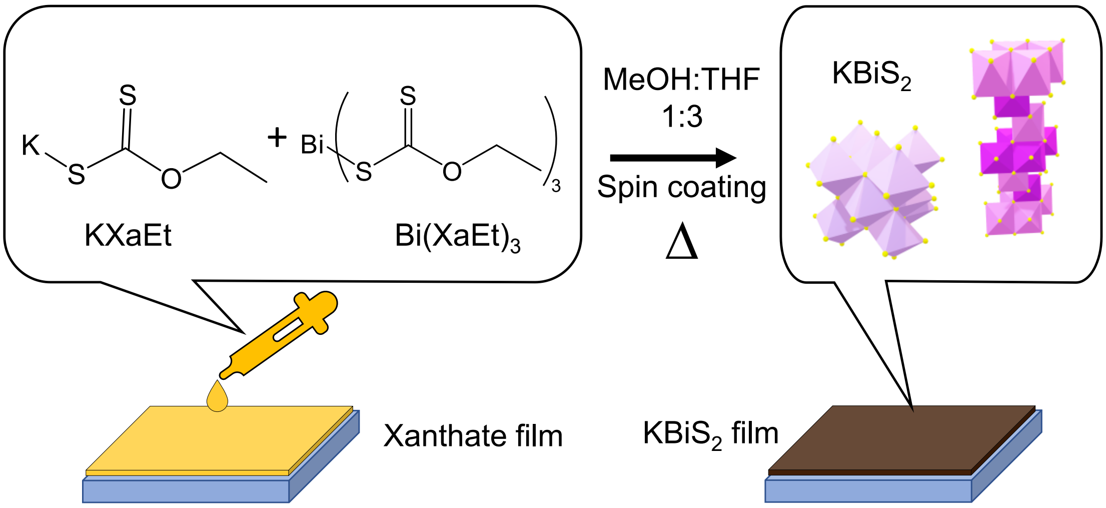


Fig. S1 Schematic depiction of the $KBiS_2$ thin film preparation.

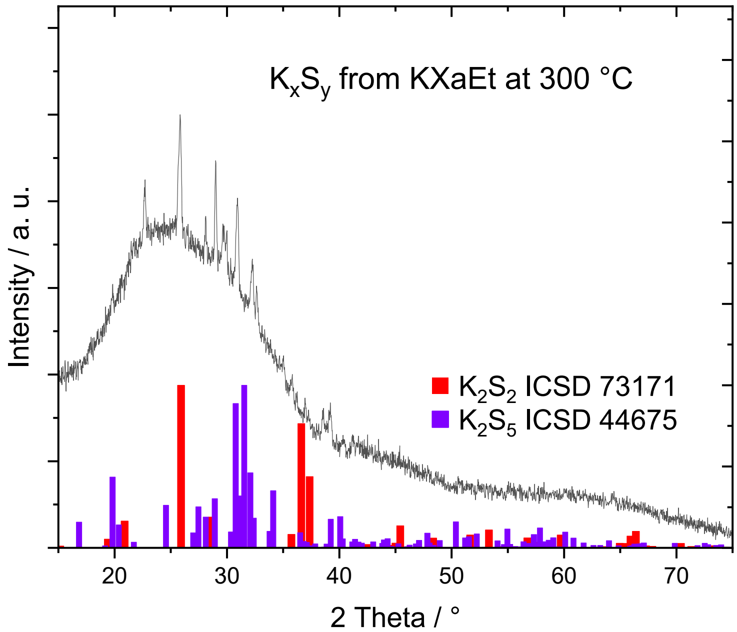


Fig. S2 X-ray diffractogram of a KXaEt thin film prepared at 300 °C on glass with two potassium sulfide reference patterns.

Table S1 Primary crystallite sizes of $KBiS_2$ formed from different precursor ratios and at different temperatures estimated with the Scherrer equation

Sample	Primary crystallite size / nm
KBS_1.5 200 °C	10 ± 2
KBS_1.5 250 °C	15 ± 2
KBS_1.5 300 °C	23 ± 4
KBS_1.5 350 °C	29 ± 7

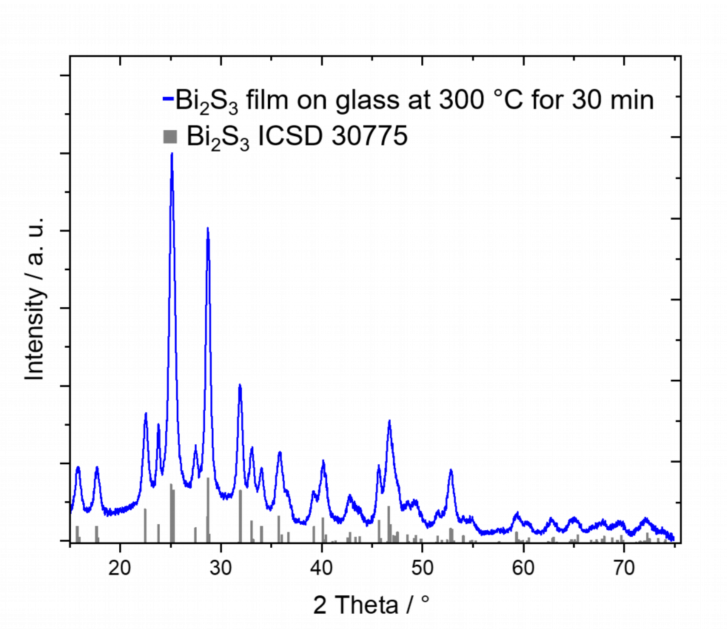


Fig. S3 Bi_2S_3 film on glass prepared from $Bi(XaEt)_3$ annealed at 300 °C for 30 min (blue line) with the orthorhombic Bi_2S_3 (ICSD 30775) as reference pattern (grey columns).

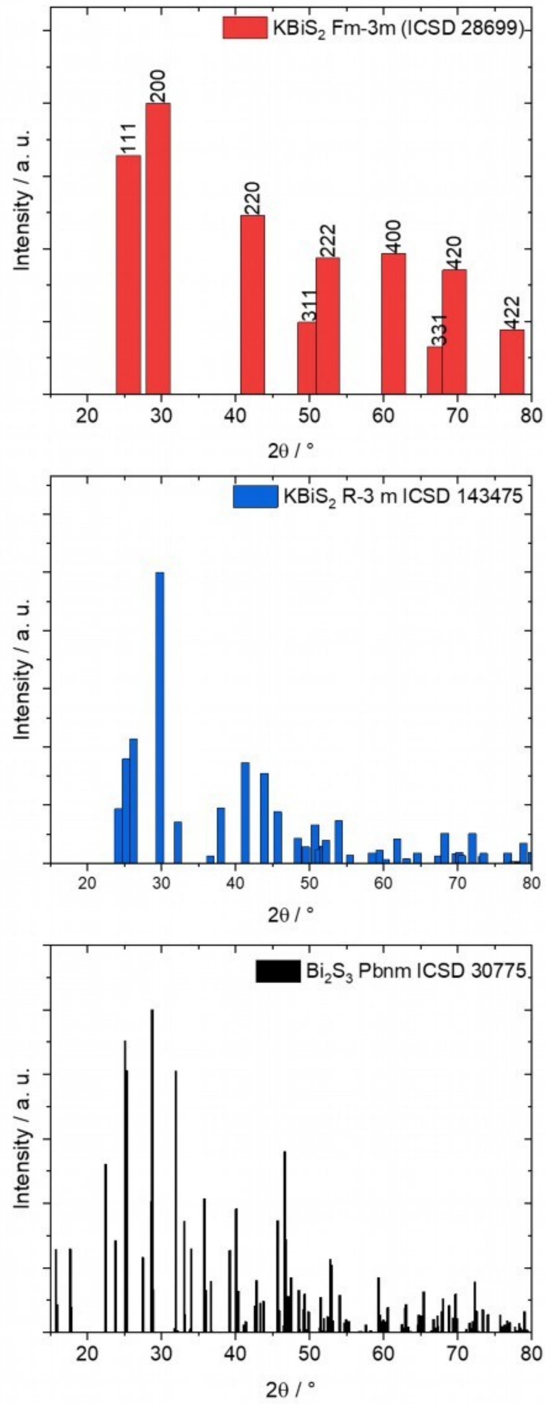


Fig. S4 Reference diffractograms for cubic $KBiS_2$ (ICSD 28699)[1], rhombohedral $KBiS_2$ (ICSD 143475)[2] and orthorhombic Bi_2S_3 (ICSD 30775).[3]

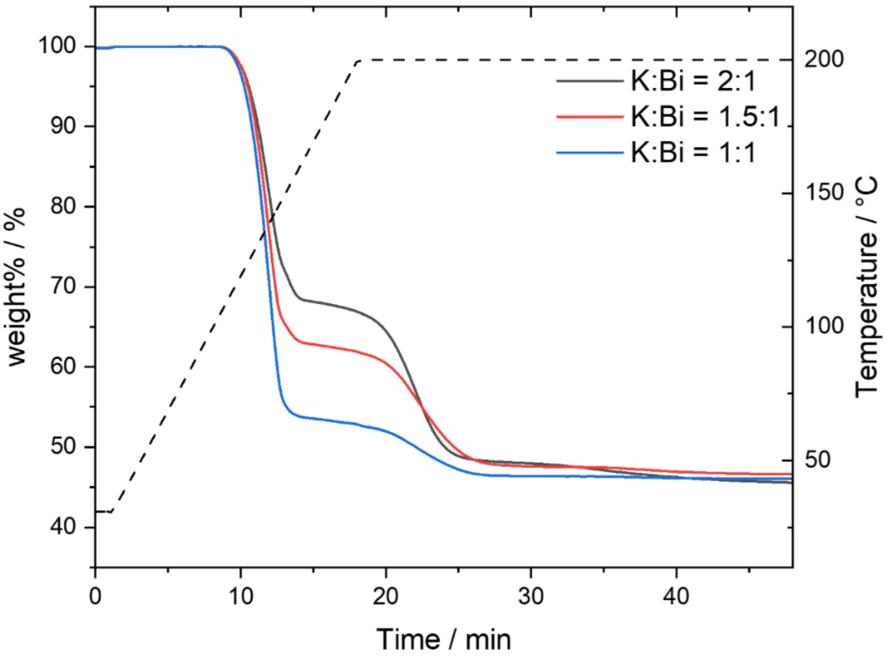


Fig. S5 TGA curves of KXaEt/Bi(XaEt)$_3$ mixtures up to 200 °C and holding for 30 min.

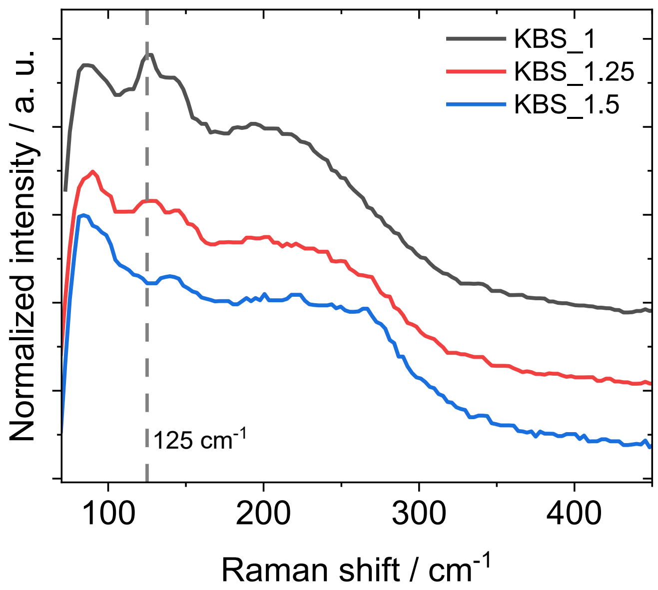


Fig. S6 Raman spectra of the samples KBS_1, KBS_1.25 and KBS_1.5.

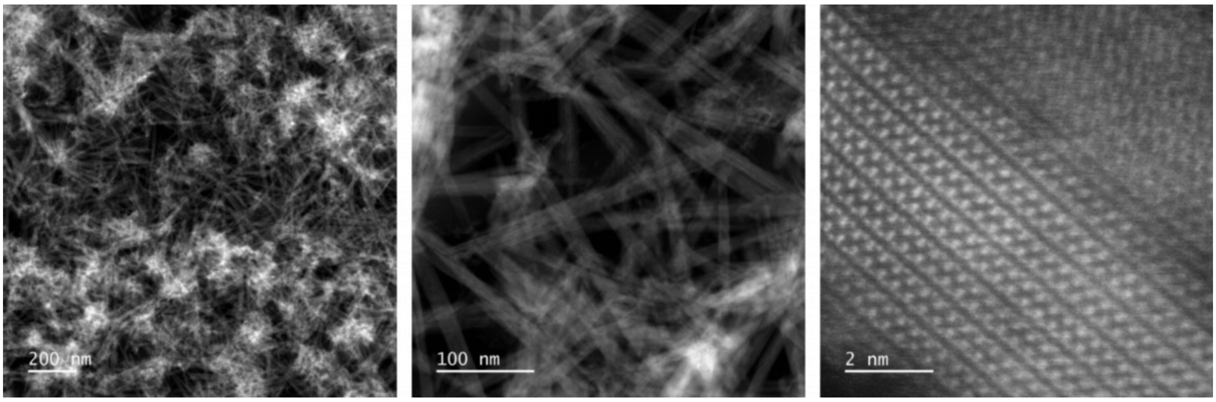


Fig. S7 STEM images at different magnifications of KBS_1.

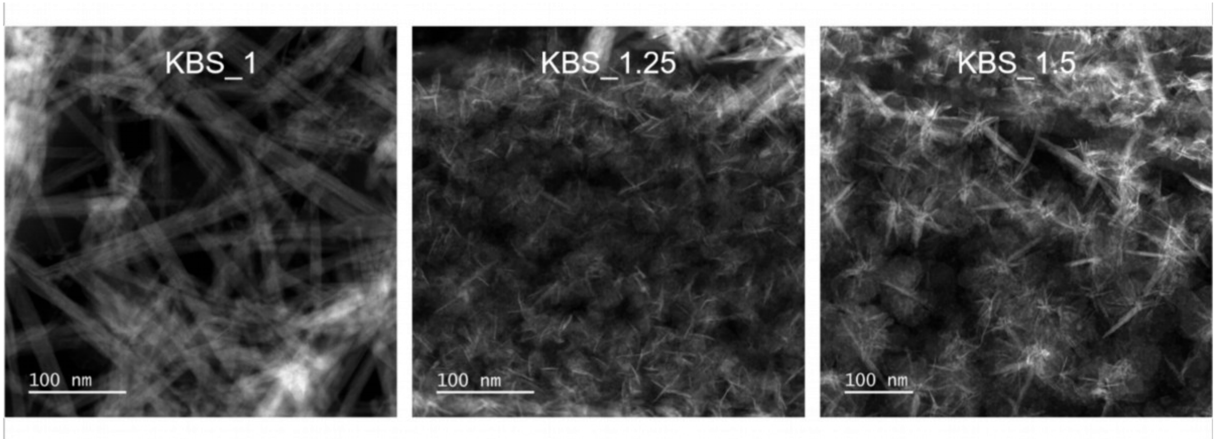


Fig. S8 TEM images of KBS_1, KBS_1.25 and KBS_1.5.

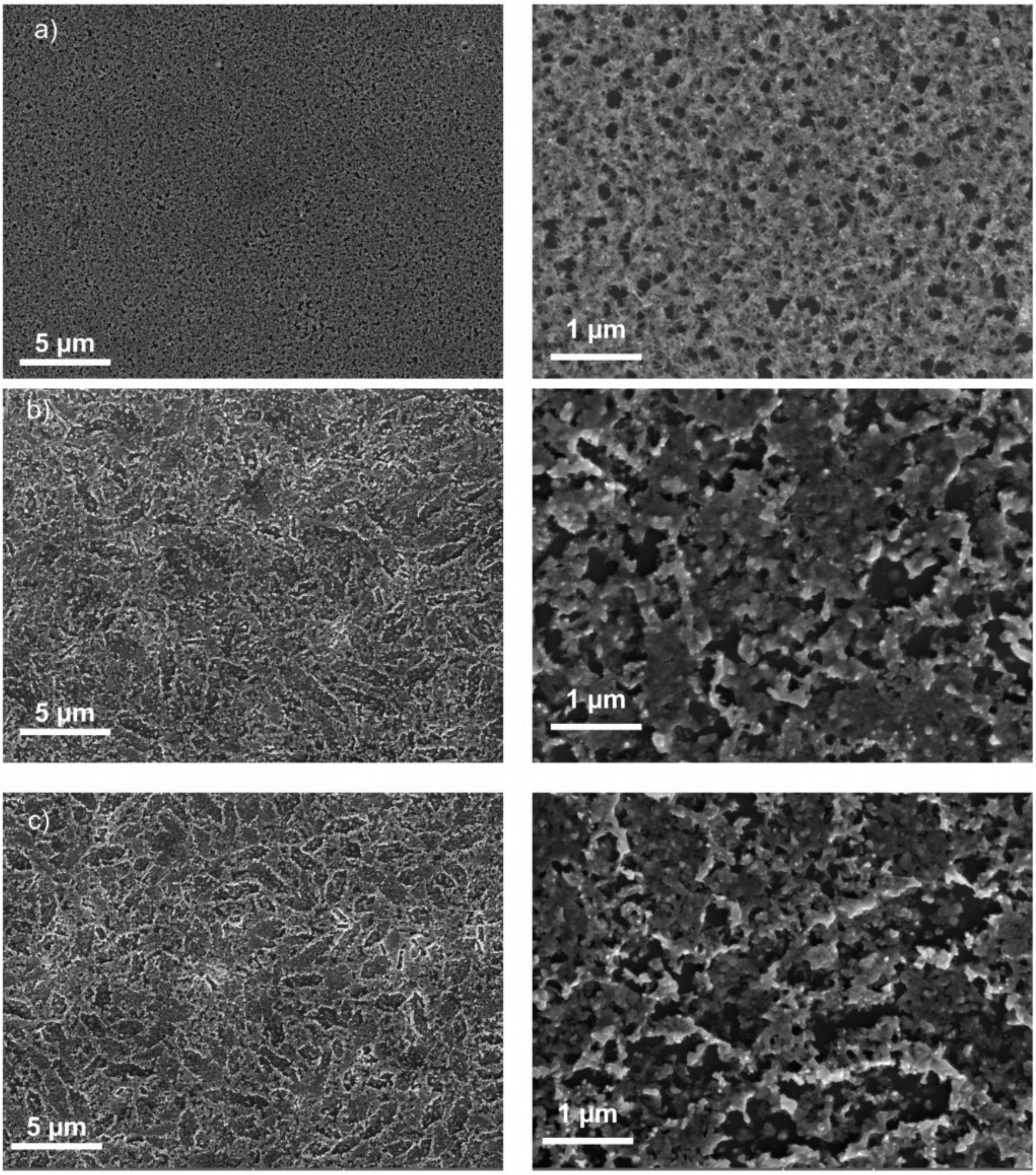


Fig. S9 SEM images at different magnifications of a) KBS_1, b) KBS_1.5 and c) KBS_2 (K:Bi = 2:1).

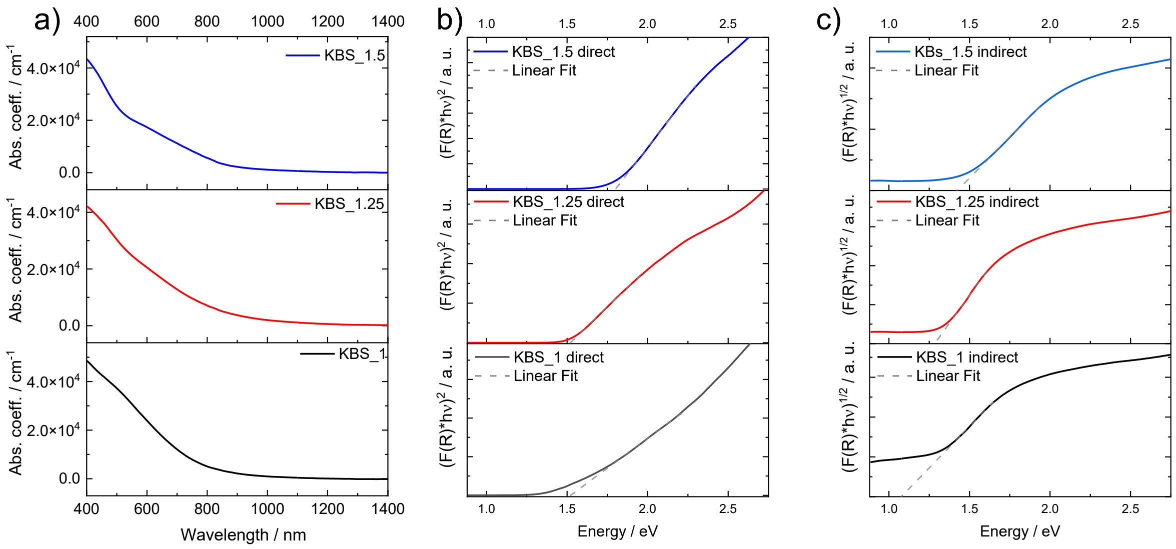


Fig. S10 a) Absorbance spectra of thin film samples on glass; corresponding Tauc plots of the drop coated thick films with the Kubelka-Munk method[4] for b) direct bandgaps and c) indirect bandgaps.

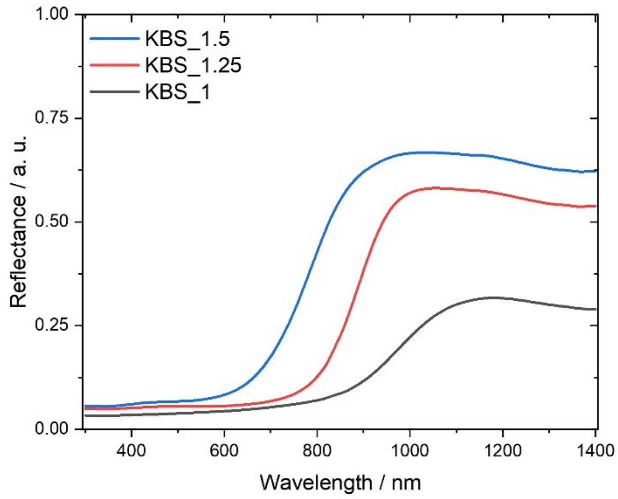


Fig. S11 Reflectance spectra of the samples KBS_1, KBS_1.25 and KBS_1.5.

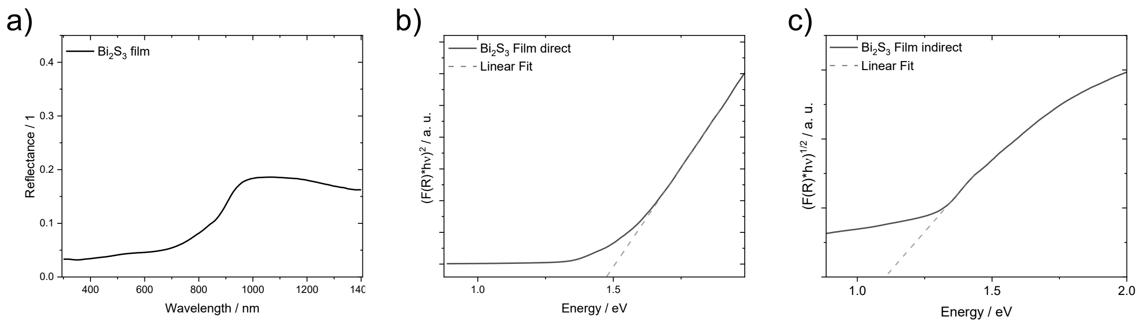


Fig. S12 a) Reflectance spectrum, b) Tauc-plot for direct and c) indirect bandgap of a Bi_2S_3 film, corresponding to bandgaps of 1.52 eV (direct) and 1.10 eV (indirect).

Table S2 Optical bandgaps obtained from the Kubelka-Munk method and Tauc plots and values from the literature

	Direct optical bandgap / eV	Indirect optical bandgap / eV
Bi_2S_3 Film	1.50	1.10
KBS_1 Film	1.52	1.04
KBS_1.25 Film	1.52	1.29
KBS_1.5 Film	1.80	1.42
Bi_2S_3 [a]	1.29[5]	1.25[6]
$KBiS_2$ (cubic) [a]	1.61[7]	-
$KBiS_2$ (rhomb.) [a]	-	1.21[2,8]

[a]Literature values

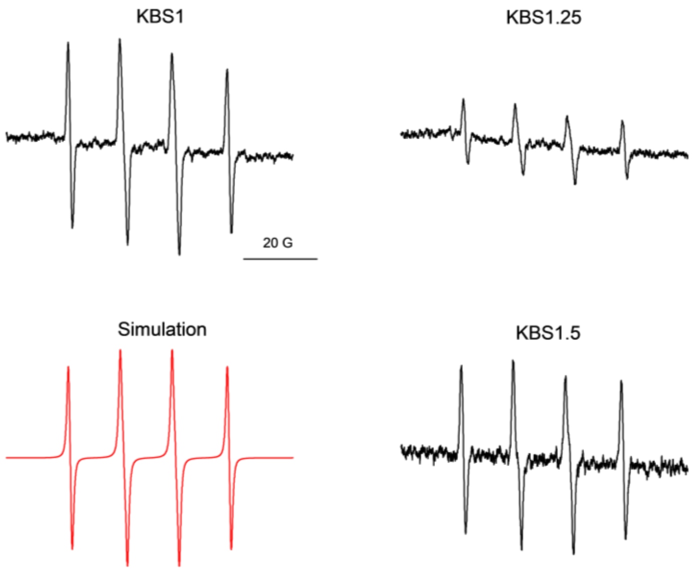
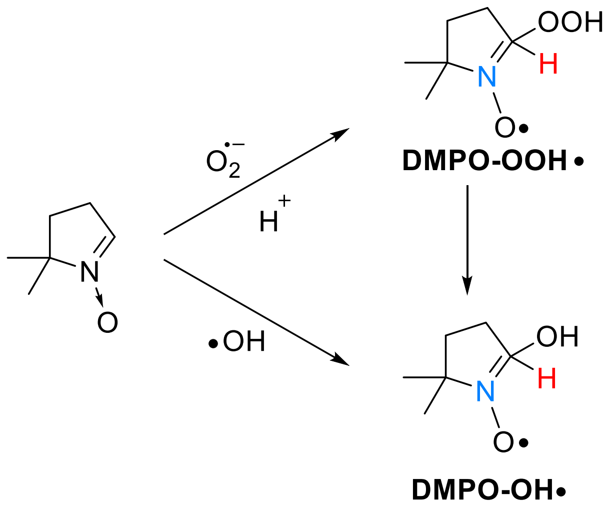


Fig. S13 EPR spectra obtained after the irradiation (405 nm, 600 s) of KBS_1, KBS_1.25, and KBS_1.5 with DMPO as spin-trap in the presence of atmospheric oxygen. The red line shows the simulated EPR spectrum (aN = 14.3 G, aH = 14.3 G).



Scheme S1 Reactions between DMPO and superoxide and hydroxyl radicals. Nuclei with observable EPR hyperfine coupling constants are shown in color.

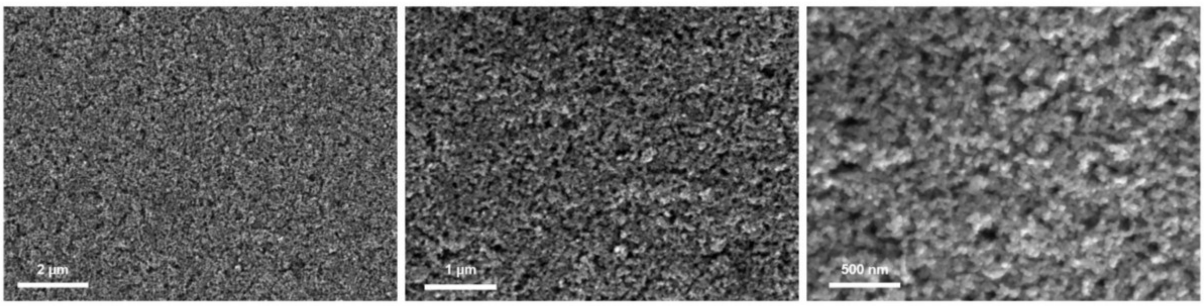


Fig. S14 SEM images of a mp-TiO_2 film sensitized with KBS_1.5 in different magnifications.

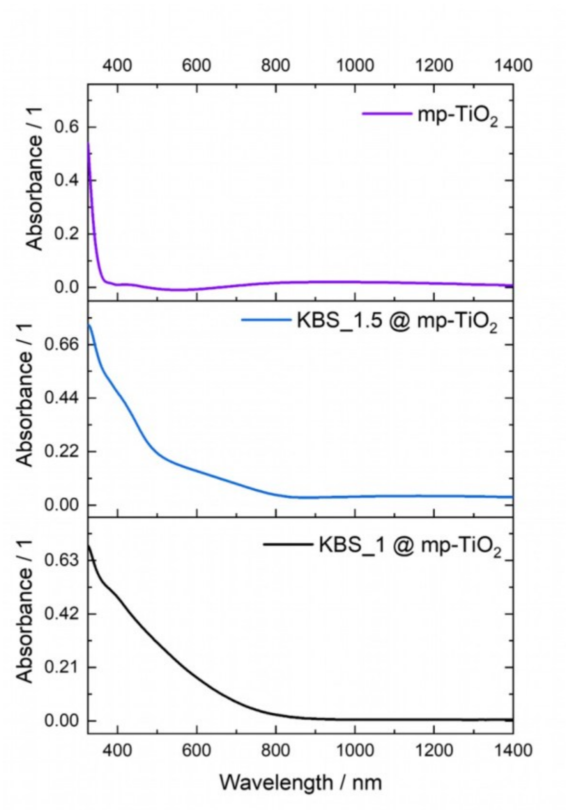


Fig. S15 Absorbance spectra of mp-TiO_2 and $KBiS_2$ sensitized mp-TiO_2.

Table S3 Stretch exponential fitting parameters for the TAS data

TiO_2/KBS/Spiro	
Model	TAS_FIT (User)
Equation	A*exp(-(x/t)^b)
Plot	L
A	6.22527E-4 ± 9.96829E-6
b	0.29162 ± 0.00368
t	3.73698E-5 ± 2.11415E-6
Reduced Chi-Sqr	1.39286E-10
KBS/Spiro-OMeTAD	
Model	TAS_FIT (User)
Equation	A*exp(-(x/t)^b)
Plot	P
A	5.624E-5 ± 3.67967E-6
b	0.22973 ± 0.01691
t	0.00129 ± 4.22484E-4
Reduced Chi-Sqr	1.2447E-10
TiO_2/KBS	
Model	TAS_FIT (User)
Equation	A*exp(-(x/t)^b)
Plot	R
A	0.00775 ± 0.02284
b	0.04237 ± 0.02251
t	4.72341E-23 ± 1.58868E-21
Reduced Chi-Sqr	1.20823E-10

References

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