Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information

Cation exchange synthesis of $AgBiS_2$ quantum dots for highly efficient solar cells

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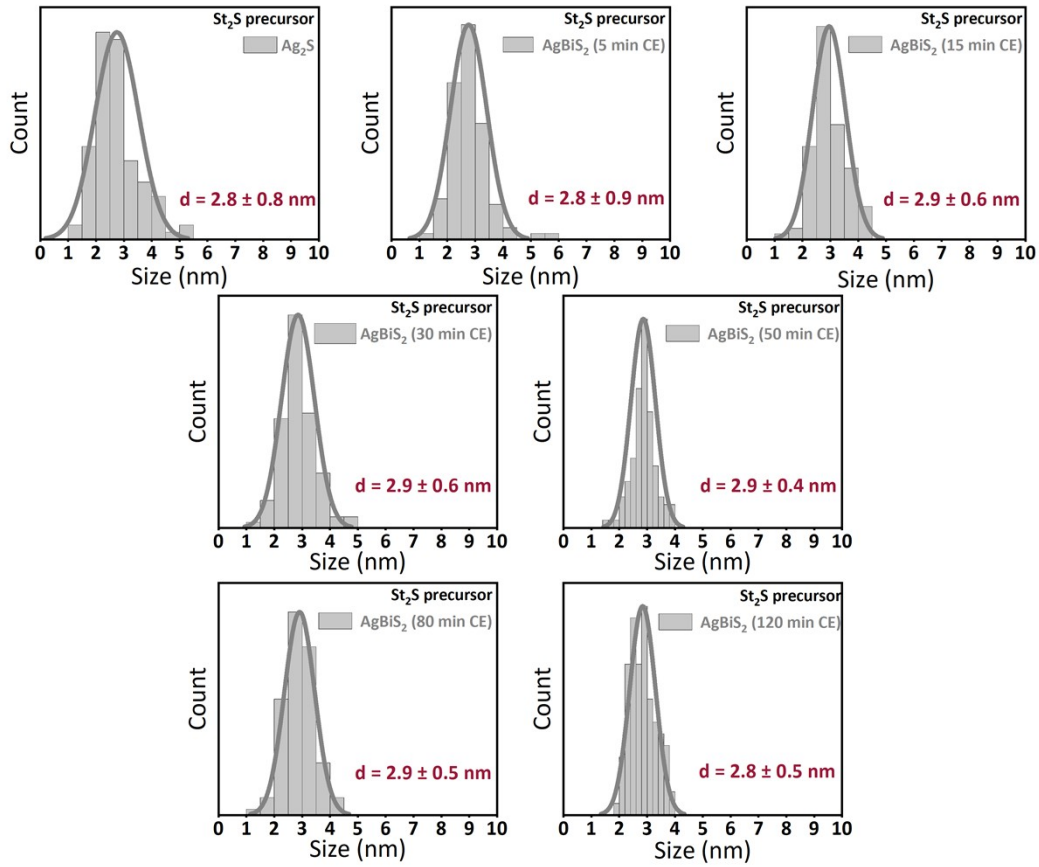

Figure S1. Particle size distribution of $AgBiS_2$ synthesized with St_2S at different reaction times of cation exchange.

Table S1. Relative atomic percentages and ratio (XPS) for Ag_2S and $AgBiS_2$ at different reaction times.

	Ag, %	**Bi, %**	**S, %**	**Ag:Bi:S ratio**
Ag_2S	1.14	-	0.55	2.1:1
5 min	11.18	5.44	8.64	1.3:0.6:1
15 min	7.59	6.54	8.88	0.9:0.7:1
30 min	5.64	4.95	6.25	0.9:0.8:1
50 min	8.19	6.53	9.76	0.8:0.7:1
80 min	6.9	5.61	8.41	0.8:0.7:1
120 min	9.06	7.15	12.15	0.8:0.6:1

Table S2. Atomic ratio (XPS) for $AgBiS_2$ synthesized with cation exchange and hot-injection methods.

	Ag:Bi:S ratio	**reference**
$AgBiS_2$-St_2S (CE synthesis)	0.8:0.6:1	This work
$AgBiS_2$-St_2S (Hot-injection synthesis)	1.7:0.3:1	[1]
$AgBiS_2$-TMS_2S (Hot-injection synthesis)	1.2:0.7:1	[1]
$AgBiS_2$-TMS_2S (Hot-injection synthesis)	1.5:1.0:1.6	[2]

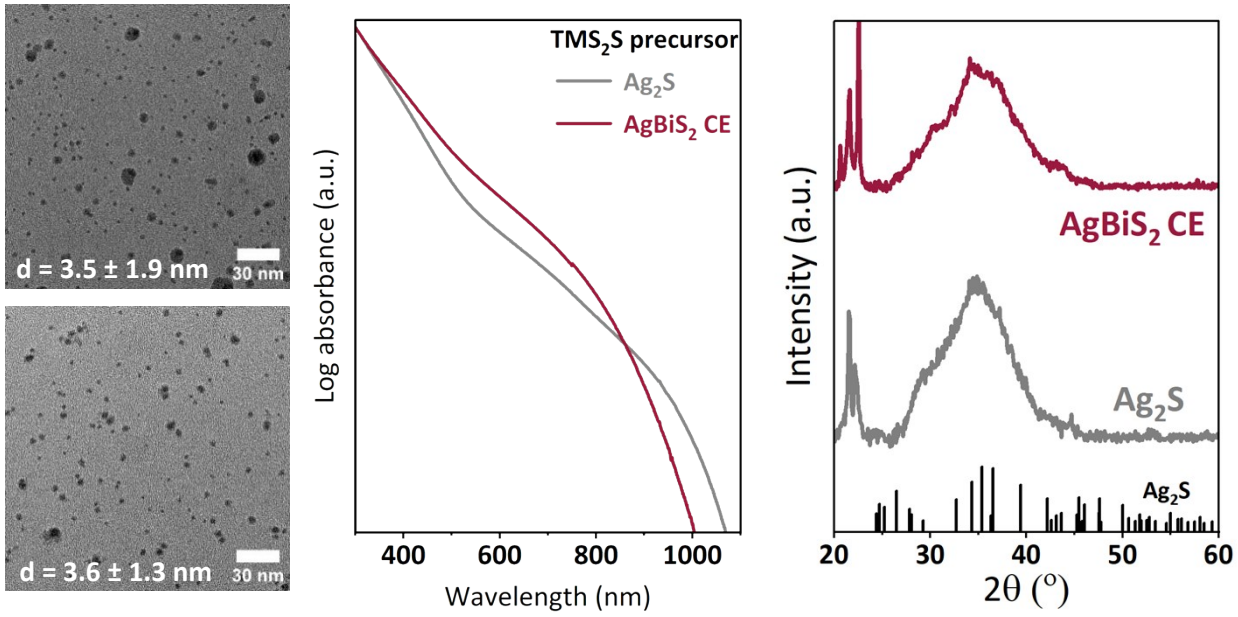

Figure S2. TEM images before exchange (top) and after exchange (bottom), absorbance spectra and XRD patterns of Ag_2S and $AgBiS_2$ synthesized with TMS_2S precursor.

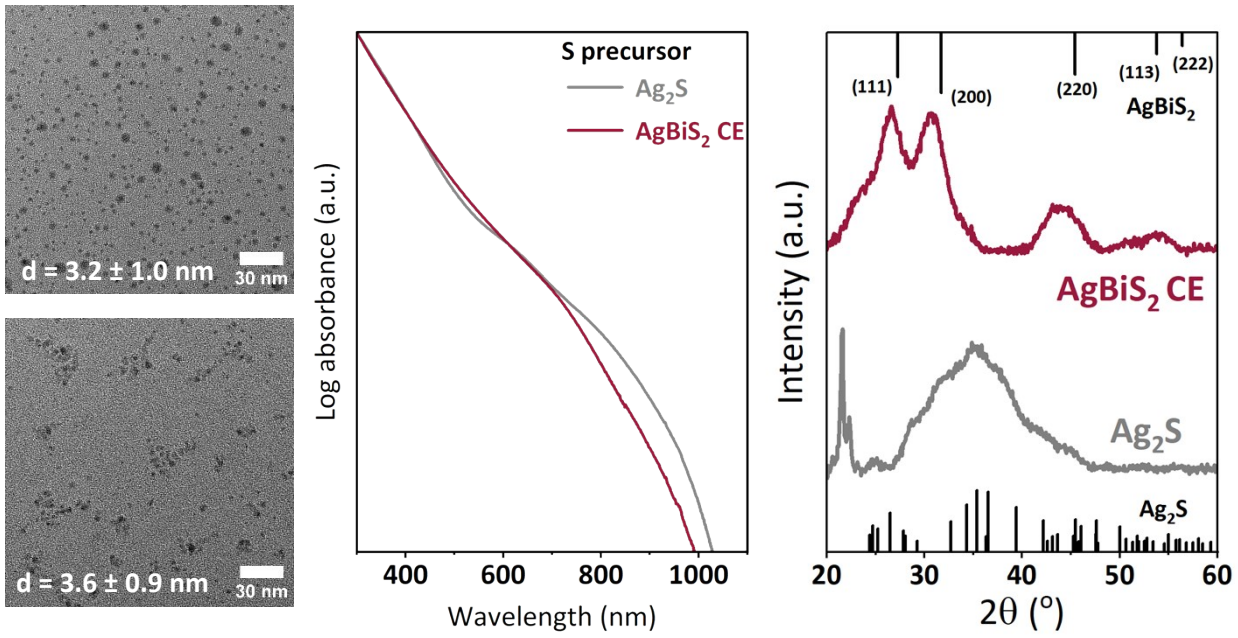

Figure S3. TEM images before exchange (top) and after exchange (bottom), absorbance spectra and XRD patterns of Ag_2S and $AgBiS_2$ synthesized with S precursor.

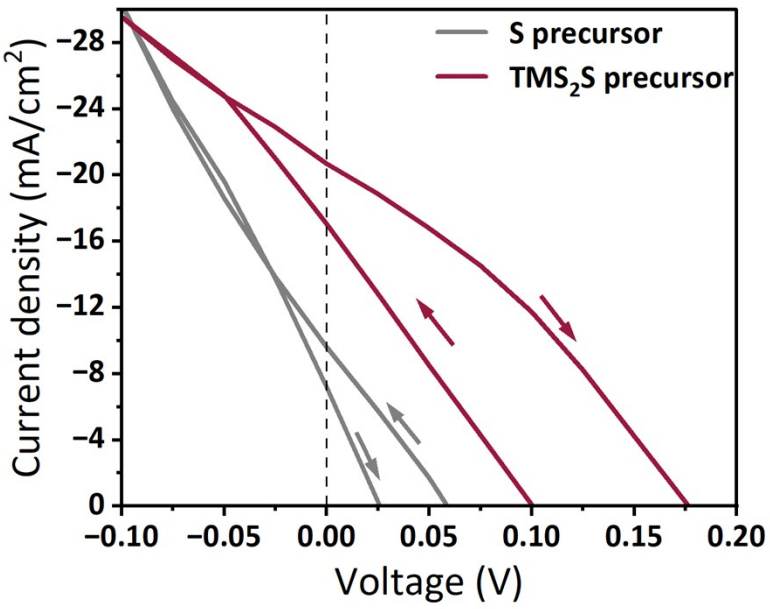

Figure S4. *J–V* curves (forward and reverse scanning) of devises based on $AgBiS_2$ synthesized with S and TMS_2S precursors.

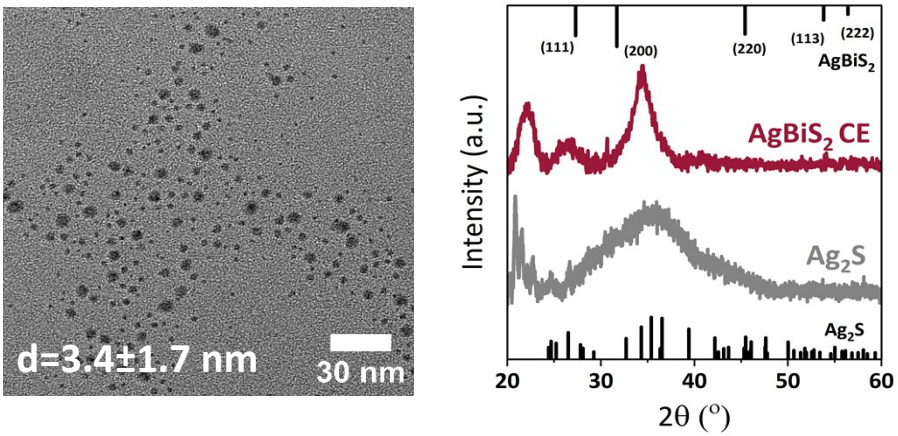

Figure S5: Left: TEM image of larger Ag_2S QDs (>3 nm average size) used for the cation exchange reaction. Right: XRD pattern of the initial larger Ag_2S QDs and the material after 120 min cation exchange at 50 °C with $Bi(neo)_3$. A complete conversion into high-quality $AgBiS_2$ cannot be achieved for such QDs.

Table S3. Averaged photovoltaic parameters of Ag_2S and $AgBiS_2$ based solar cells.

	V_{oc} (V)	J_{sc} (mA/cm²)	FF (%)	PCE (%)
0 min	0.246±0.060	2.65±0.91	0.37±0.06	0.27±0.18
Champion device	0.331	3.95	0.45	0.58
30 min	0.478±0.008	15.28±1.58	0.43±0.08	3.31±0.70
Champion device	0.478	16.98	0.52	4.27
120 min	0.484±0.004	23.07±1.03	0.61±0.02	6.76±0.53
Champion device	0.486	23.81	0.64	7.35

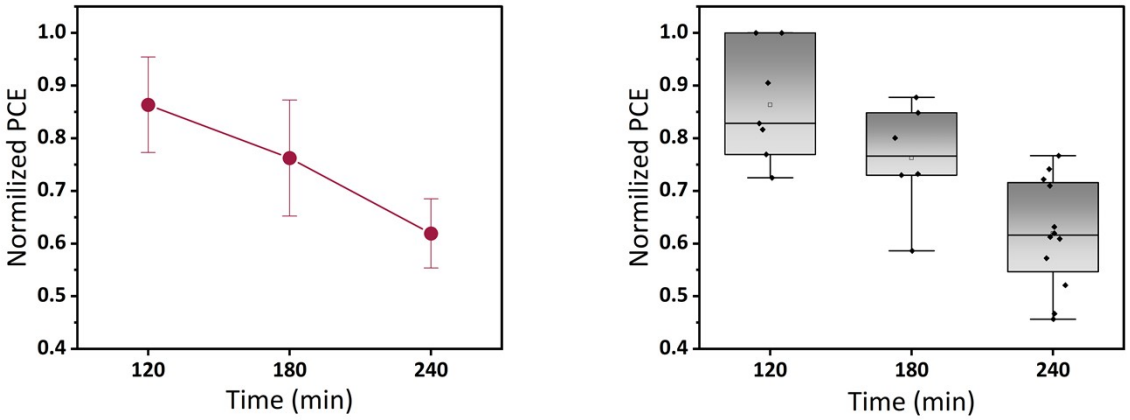

Figure S6: Performance Evaluation of the solar cell efficiency (PCE) for longer cation exchange times (normalized to the best performing solar cell.)

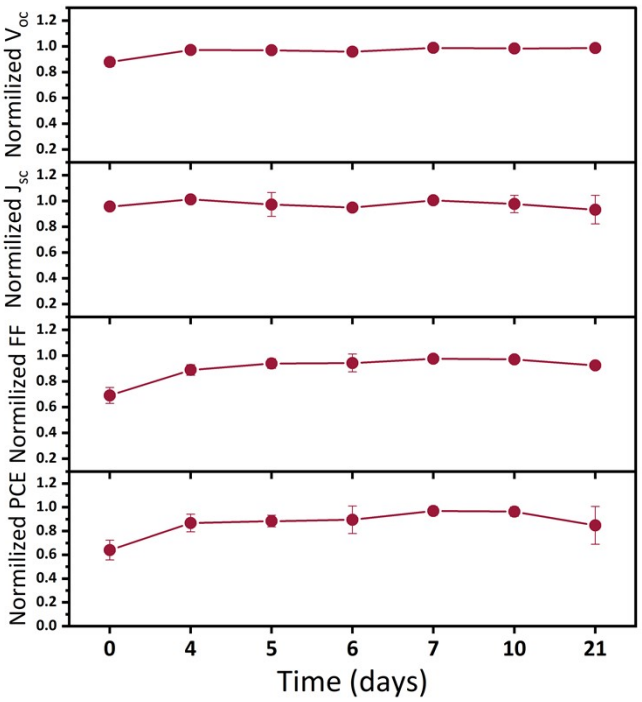

Figure S7: Evolution of the solar cell parameters and performance upon storage in ambient and electrical measurements on day 0 (directly after fabrication), day 4, 5, 6, 7, 10, and 21.

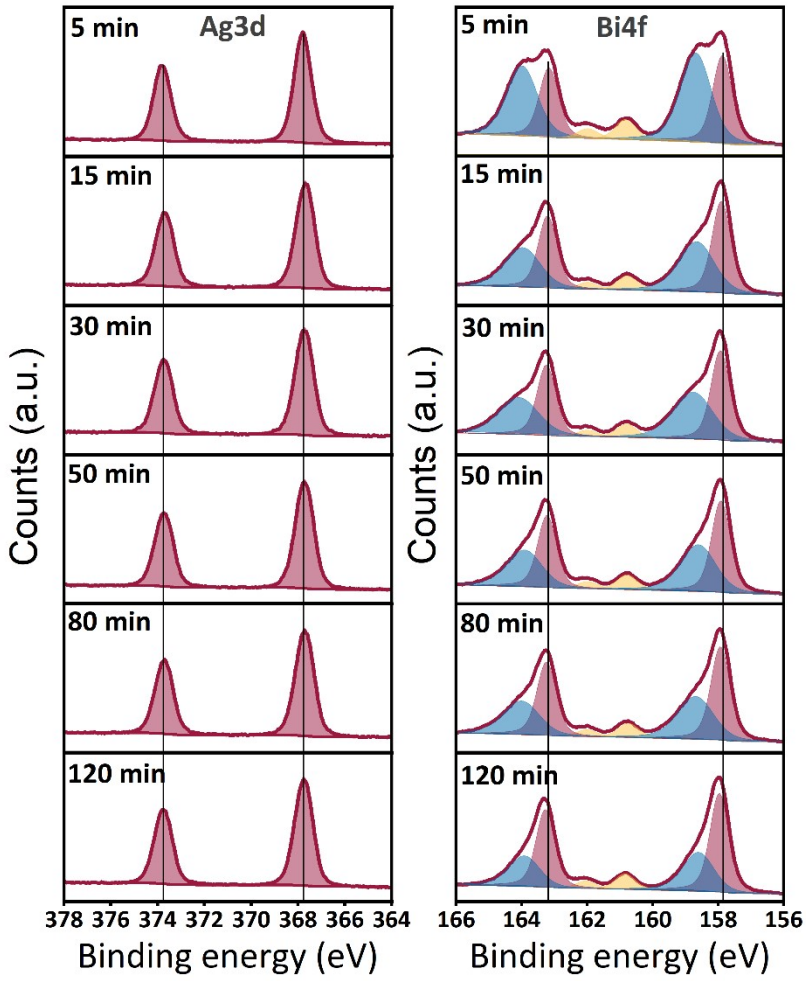

Figure S8. XPS spectra of Ag 3d (left column) and Bi 4f and S 2p (right column) for different times of cation exchange.

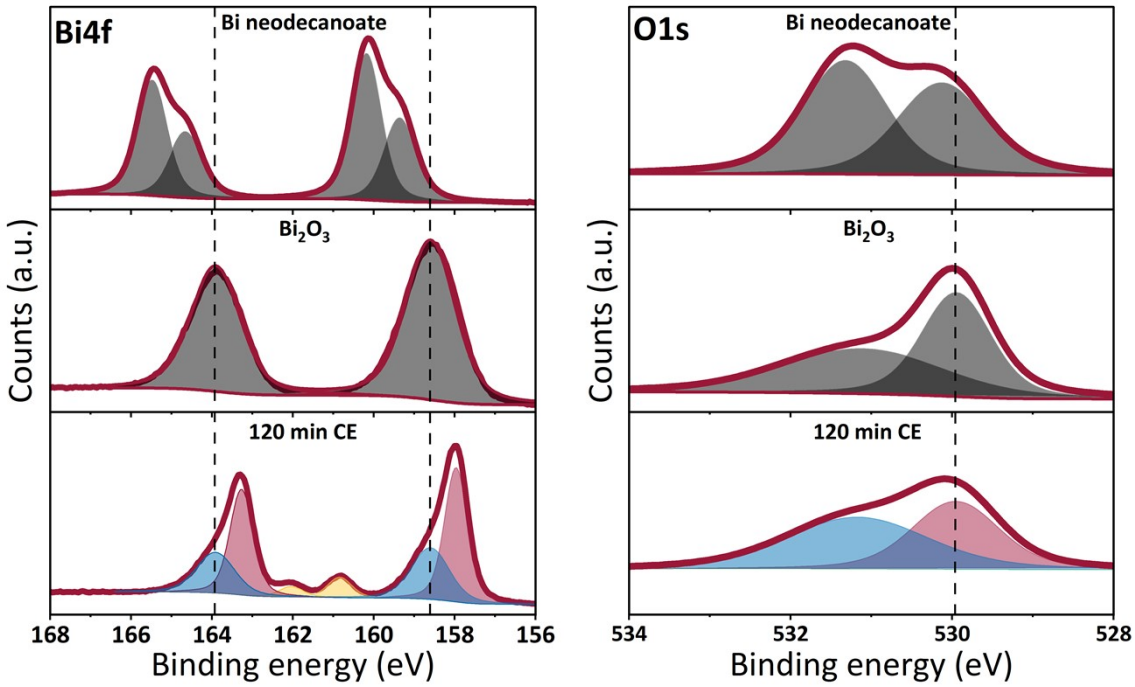

Figure S9: Left panel: XPS data for Bi 4f (left panel) and O 1s (right panel) of $Bi(neo)_3$ precursor, Bi_2O_3 and $AgBiS_2$ nanocrystals after 120min of cation exchange (CE).

References

1. Albaladejo-Siguan, M. *et al.* Bis(stearoyl) Sulfide: A Stable, Odor-Free Sulfur Precursor for High-Efficiency Metal Sulfide Quantum Dot Photovoltaics. *Advanced Energy Materials* vol. 13 at https://doi.org/10.1002/aenm.202203965 (2023).
2. Bernechea, M. *et al.* Solution-processed solar cells based on environmentally friendly AgBiS2 nanocrystals. *Nat. Photonics* **10**, 521–525 (2016).